EXPERIMENTAL DETERMINATION OF THE SOLUBILITY OF SMALL ORGANIC MOLECULES IN H_2O AND D_2O AND THE APPLICATION OF THE SCALED PARTICLE THEORY TO AQUEOUS AND NONAQUEOUS SOLUTIONS

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Date Approved by Chairman: 15 August 1974

DEDICATION

This dissertation is dedicated to A., B., C., and D. That part of the alphabet that has special significance to the author.

ACKNOWLEDGEMENTS

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SUMMARY

The solubilities of benzene, toluene, pentane, cyclohexane, cyclopentene, cyclohexene, 1,4-cyclohexadiene, and cycloheptatriene in H_2O and D_2O were determined over the temperature range 278°K to 318°K, using gas-liquid chromatographic techniques.

The Henry's Law constants determined from the solubility data were used to obtain the thermodynamic changes associated with the solution process. The thermodynamic properties for the transfer of the solute from H_2O to D_2O have been evaluated.

In addition the partial molar volumes of some aromatic alcohols in H_2O have been determined using a magnetic float densimeter.

The scaled particle theory of solutions has been extended to evaluate interaction partial molar quantities, solvent and solute hard core diameters, and solvent and solute interaction parameters. Extensive calculations of solution properties of both polar and non-polar solvent systems have been carried out and are reported. The theory has been extended to the solvent D_2O and has been used to predict transfer properties of solutes from H_2O to D_2O.

Most of the available literature data pertaining to H_2O and D_2O acting as both the solvent and solute are tabulated. The theoretically predicted thermodynamic properties for these and other systems are compared to the experimentally obtained values.

Various data correlations have been developed using the scaled particle theory which enable the prediction of thermodynamic solution

properties and molecular properties.

CHAPTER I

INTRODUCTION

Solutions and solution properties have been of considerable interest, both experimentally, and theoretically, for a great many years[1-18]. The interest stems from the desire to determine how the structure or properties of the solution are altered by the interaction of the solute and solvent. Armed with the knowledge of how the solution is affected by the interaction of the solute and solvent it should be possible to formulate a theory which will be capable of predicting properties of a large number of different solute-solvent systems.

If we were to try to rank in importance the substances required to sustain life, water would probably rank among the most crucial. Man is dependent upon water in a great many ways, among which are the sustaining of metabolic processes, the production of food stuffs, the operation of industrial capacity, the use of as recreational facilities, the supplying of drinking water, and many other uses. The available supplies of fresh water are being polluted rapidly and are causing national and international[28-33] problems. The result has been the development of increased interest in measurement and removal of pollutants from water.

In the areas of medical research there is a continued interest in the aqueous environment with regard to how it affects the properties of molecules such as proteins. These effects are manifest in changes of hydrophobic bonding and biological activity[19-27].

The study of the properties of dilute solutions are particularly

useful to the understanding of the nature of the solution process. Dilute solutions are solutions in which the solubility of a substance is directly proportional to either the pressure or the activity of the dissolved substance. Such solutions are said to obey Henry's Law and it can be shown that for such solutions the only molecular interactions of importance are those involving the interactions of single solute molecules with the solvent. Thus experimental and theoretical studies of solutions obeying Henry's Law give direct information about the single solute molecule-solvent interaction.

Of the early experimental investigations of systems involving water the work of Butler et al. is of particular significance[1-5]. These studies involved non-electrolyte-water systems and it was noted by the investigators that a steady decrease of solubility occurs with increasing number of carbon atoms in an homologous series of organic compounds. It was also noted that while appreciable solubility is conferred by hydrophilic groups the solubility decreases in a steady manner as the length of hydrocarbon chain increases. Thus, they deduced that the free energy of hydration was approximately an additive function of the groups present in the solute molecule. Further,they noted that the enthaply of hydration was not the predominant factor determining the free energy of hydration and that the free energy and enthalpy of hydration changed in opposite directions; thus the entropy of hydration changes considerably in going from one compound to another. A great many other investigators have contributed to the literature of aqueous solutions since Butler's work and many of these shall be referred to in other chapters.

The most significant early contributions made to the theoretical aspects of water solutions[6] and solutions[7] in general were made in 1939 by Eley where he formally described the solution process as one consisting of two steps (as did Uhlig[34]), the first involving creating a cavity in the solvent large enough to accommodate the solute molecule (work expended) and the second involving the introduction of the solute into this cavity (molecular solute-solvent interaction). Since that time various other theories of solutions[35-46] have been proposed the most successful of which has been that based upon the scaled particle theory of fluids[44-49].

The present study is aimed at determining the Henry's Law solubility as a function of temperature of a number organic hydrocarbons in H_2O and D_2O. The thermodynamic properties of the solutions are to be obtained from these temperature dependence studies. Also the partial molar volumes at infinite dilution of a number of substituted benzene derivatives are to be determined. In addition to the experimental studies, a theoretical study will be made relating the thermodynamic properties to the molecular properties of the solutes and of water and D_2O using a form of the scaled-particle theory of solutions developed by Pierotti[51-53]. The theory will be used to determine effective interaction parameters and effective hard core diameters of a large number of solvents. The theory will be improved by assuming the averaged molar interaction energy is equivalent to the molar free energy,allowing the evaluation of the enthalpy, entropy , and volume of interaction, which in turn allows one to evaluate of the partial

molar entropy and volume of solution.

CHAPTER II

THEORETICAL

There are a large number of theories[37-53,56-66] dealing with the solubility of non-polar molecules in various solvents including water. Of the theories, the regular solution[56-58] theory, which is thermodynamic in nature, does not describe the behavior of water solutions. Other theories have been developed specifically to describe the behavior of water solutions but depend upon models which ascribe a structure to water[38-40,61-66]. To date the most successful general theory of solutions is probably that based upon the scaled particle theory of fluids[41-50]. This theory makes it possible to calculate the reversible work required to introduce a spherical particle into a fluid of spherical particles. In 1963 and 1965 Pierotti[51-53] proposed a form of the scaled particle theory applied to real systems, in which the attractive intermolecular interaction is treated as a perturbation to the treatment of hard spheres. This theory depends only upon the molecular properties of the solute and solvent, and appears to work equally well for all solvents. This fact was indicated in the original work of Pierotti[51-53] and the recent work of DeLigny and van der Veen[67].

In this chapter the theory for the solubility of non-polar substances in liquids will be developed, and then it will be extended to solutions of non-polar substances in water and D_2O.

Solution Equilibria

The concentration of a solute dissolved in a liquid solvent can be expressed as a power series in the activity or fugacity of the solute. The power series can be expressed as[68,69]

$$\rho_2 = B_2 [f_2/kT] + B_3 [f_2/kT]^2 + \ldots \qquad (2\text{-}1)$$

where ρ_2 is the number density of the solute, f_2 is the fugacity of the solute, k is the Boltzman constant, T is the absolute temperature and the B_i 's are functions of temperature. It is possible to relate the quantities B_2, B_3, . . ,B_{i+1} to the molecular properties of the solute and the solvent utilizing the techniques of statistical mechanics. The coefficients of the terms in (f_2/kT) are called virial coefficients and in particular B_2 is the second solute-solvent virial coefficient, B_3 is the third solute-solvent virial coefficient, etc., and B_i is the i-th solute-solvent virial coefficient.

In an expression similar to equation 2-1 McMillan and Mayer[70] treated the general problem of osmotic equilibrium and showed that the osmotic pressure of a solution could be expressed in a form analogous to the virial equation of state of gases. They showed that the virial coefficients could be expressed in terms of integrals involving the configurations of one, two, etc., solute molecules and the configurations of the various molecules of the solvent. These integrals are known as configuration integrals and are of great importance in statistical mechanical treatments of equilibrium thermodynamics. Of particular importance are the configuration integrals related to B_2 and B_3. It can be shown that[54]

$$B_2 = (1/V)\int_{\text{volume}} (e^{-W(\bar{r}_i)/kT} - 1)\, d\bar{r}_i \qquad (2\text{-}2)$$

where $\bar{r}_i$ is the position of the i-th solute molecule under consideration, $W(\bar{r}_i)$ is the average potential energy of the i-th solute molecule whose center is at $\bar{r}_i$ and which interacts with the solvent. The averaging is over all allowable configurations of the solvent. The integration is over the entire volume of the solution. The importance of this coefficient is that it is dependent upon only one solute molecule interacting with the solvent and therefore excludes solute-solute interactions from entering into the first term of the expansion given by equation 2-1.

The integral expressing B_3 is considerably more complex than that for B_2 and is given by[54]

$$B_3 = (2B_2^2/\bar{V}) \iint_{\text{volume}} (e^{-\omega_2 (\bar{r}_i, \bar{r}_j)/kT} - 1) \, d\bar{r}_i d\bar{r}_j \qquad (2\text{-}3)$$

where B_2 is the second solute-solute virial coefficient, $\omega_2(\bar{r}_i, \bar{r}_j)$ is the effective pair potential of two solute molecules one located at position $\bar{r}_i$ and the second located at position $\bar{r}_j$. This effective pair potential is averaged over all configurations of the solvent molecules. The importance of B_3 is that it is dependent only upon the interaction of two solute molecules with each other and with the solvent. It can also be shown that the i-th virial coefficient is dependent upon i-molecules of solute interacting with each other and simultaneously with the solvent.

It is evident from the foregoing that the complex problem of solution equilibrium can be decomposed into its simplest parts and these can be studied independently. This study is concerned with a detailed examination of the effect of molecular type and temperature upon the second solute-solvent virial coefficient B_2, is directly

related to the experimental quantity called the Henry's Law constant.

Henry's Law is usually expressed as

$$f_2 = K\, X_2 \tag{2-4}$$

where f_2 is the fugacity of the solute, K is the Henry's Law constant and X_2 is the mole fraction of solute in the solution. Since the number density of solute molecules dissolved in a dilute solution is related to X_2 by

$$\rho_2 \bar{V}_1 = N_o X_2 \tag{2-5}$$

where $\bar{V}_1$ is the molar volume of solvent and N_o is Avogadro's number, it is evident that

$$K = RT/\bar{V}_1 B_2 \tag{2-6}$$

or

$$\ln K = \ln[RT/\bar{V}_1] - \ln B_2 \tag{2-7}$$

Since B_2 represents the probability that a molecule of solute is found at the position r_i, integrated over all possible positions in the solvent volume, it can be directly related to the Boltzman equation

$$B_2 = e^{-\bar{G}_2/RT} \tag{2-8}$$

where $\bar{G}_2$ is the partial molar free energy of the solute or its equivalent the reversible work required to dissolve one mole of solute in an infinite amount of solvent at constant pressure and temperature. Substituting equation 2-8 into 2-7 yields

$$\ln K = \bar{G}_2/RT + \ln[RT/\bar{V}_1] \tag{2-9}$$

At this point it is worth noting the relationship between K and B_2 and between B_2 and $\tilde{G}_2$, as these relationships will be made use of in the following sections.

Scaled Particle Theory of Solutions

The Scaled Particle Theory is so named because it uses a scaling or coupling parameter which measures the size of a molecule and its potential field. The success of the theory for liquids seems to indicate that the fluid structure is primarily determined by the molecular packing which can reasonably be approximated by that of hard spheres, and that the intermolecular potential primarily influences the density of the fluid.

The chemical potential of a solute μ_2, in a very dilute solution of nonelectrolytes is given by Fowler and Guggenheim[7] as

$$\mu_2 = W + P\bar{v}_2 - kT\ln[q_2^{int}/\Lambda_2^3] + kT\ln[N_2/V] \qquad (2\text{-}10)$$

where W is the potential energy of a solute molecule in the solution relative to infinite separation, P is the hydrostatic pressure, $\bar{v}_2$ is the partial molecular volume of the solute, $V\Lambda^{-3}$ is the partition function for the translational degrees of freedom per molecule of solute, q_2^{int} is the partition function for the internal degrees of freedom per molecule of solute, N_2 is the number of solute molecules in the volume, V_1, of the solution. For very dilute solutions $V = N_1\bar{v}_1$, where N_1 is the number of solvent molecules and $\bar{v}_1$ is the partial molecular volume of the solvent, and $(N_2/N_1) = X_2$, where X_2 is the mole fraction of the solute.

The sum of the first two terms on the right hand side of equation 2-10 represents the reversible work required to introduce one solute molecule into a solution of concentration N_2/V. For very dilute solutions the reversible work required to add a solute molecule to the solution is equivalent to that of adding one molecule to the pure solvent. As demonstrated by Uhlig[34] and Eley[6,7], it is convenient to view the (solution) process of introducing the solute molecule into the solvent as a two step one.

Step 1. The creation of a cavity in the solvent large enough to accommodate the solute molecule. The reversible work or partial molecular Gibbs free energy, $\bar{g}_c$, required to do this is identical to that required to introduce a hard sphere molecule of the same radius as the cavity into solution.

Step 2. The introduction of a solute molecule into the cavity which then interacts with the solvent according to some potential law. The reversible work or partial molecular Gibbs free energy, $\bar{g}_i$, involved is identical to that of charging the hard sphere introduced or cavity created in the first step to the required potential.

Thus $\bar{g}_c + \bar{g}_i$, is equivalent to $W + P\bar{v}_2$ and since $X_2/\bar{V}_1$ is equivalent to N_2/V making the appropriate substitutions in equation (2-10) yields

$$\mu_2^{soln} = \bar{g}_c + \bar{g}_i + kT\ln (q_2^{int}/\Lambda_2^3) + kT\ln (X_2/\bar{V}_1) \qquad (2\text{-}11)$$

The chemical potential of the solute in the gas phase in equilibrium with the solution is given by the equation

$$\mu_2^{gas} = kT\ln\ (q_2^{int}/\Lambda_2^3) + kT\ln\ (f_2/kT) \qquad (2\text{-}12)$$

At equilibrium the chemical potential of the solute in the gas and solution phases are equal, thus equating (2-12) and (2-11) yields

$$\ln\ (f_2/X_2) = \bar{g}_c/kT + \bar{g}_i/kT + \ln\ (kT/\bar{V}_1) \qquad (2\text{-}13)$$

And since Henry's Law is given by $K = f_2/X_2$ equation (2-13) yields

$$\ln K = \bar{g}_c/kT + \bar{g}_i/kT + \ln\ (kT/\bar{V}_1) \qquad (2\text{-}14)$$

Replacing the molecular quantities by molar quantities yields

$$\ln K = \bar{G}_c/RT + \bar{G}_i/RT + \ln\ (RT/\bar{V}_1) \qquad (2\text{-}15)$$

A statistical mechanical theory of fluids has been developed Reiss, Frisch, Helfand, and Lebowitz[41-51] based upon the properties of the exact radial distribution functions. This theory yields an approximate expression for the reversible work required to introduce a spherical particle into a fluid of spherical particles. The system used consists of (N-1) spherical particles obeying a pairwise additive potential to which an additional spherical particle, obeying the same potential, is coupled using the procedure of distance scaling. The coupling procedure yields an expression for the chemical potential of the fluid in terms of a function related to the radial distribution function of the fluid. It is demonstrated that the radial distribution function need not be known since, for hard sphere particles, the only part of the radial distribution function which contributes to the chemical potential of the fluid is that part which determines the

number density of particles in contact with the hard sphere particle.

The partial molar Gibbs free energy, $\bar{G}_c$, of creating a cavity is given by Reiss, et al. by the following equation

$$\bar{G}_c = K_o + K_1 a_{12}^2 + K_2 a_{12}^2 + K_3 a_{12}^3 \qquad (2\text{-}16)$$

where the various K's are functions of the density, temperature, pressure and hard sphere diameter of the fluid. And where $a_{12}$is the radius of a spherical cavity which excludes the centers of solvent molecules. The K's were given by the following equations

$$K_o = RT\ \{-\ln(1-y) + 9/2[y/(1-y)]^2\} - \pi P a_1^3/6 \qquad (2\text{-}17a)$$

$$K_1 = -\ RT/a_1\ \{6y/(1-y) + 18[y/(1-y)]^2\} + \pi P a_1^2 \qquad (2\text{-}17b)$$

$$K_2 = RT/a_1^2\ \{12y/(1-y) + 18[y/(1-y)]^2\} - 2\pi P a_1 \qquad (2\text{-}17c)$$

$$K_3 = 4\pi P/3 \qquad (2\text{-}17d)$$

where $y = \pi\rho_1 a_1^3/6$ is the number density of the solvent and a_1 is the hard sphere diameter of a solvent molecule. The radius of the sphere a_{12} which excludes the centers of solvent molecules is equal $(a_1 + a_2)/2$, where a_2 is the diameter of the cavity to be created. Substituting 2-17a,b,c,d into 2-16 yields

$$\bar{G}_c = RT\left\{-\ln(1-y) + 9/2[y/(1-y)]^2 - \left[\ (a_{12}/a_1)\ \left(6y/(1-y)\right)\right.\right.$$
$$\left.\left. + 18[y/(1-y)]^2\right] + [a_{12}/a_1]^2\ \left[12y/(1-y) + 18[y/(1-y)]^2\right]\right\}$$
$$+ Pf(a) \qquad (2\text{-}18)$$

where the symbols are defined as before and Pf(a) is defined as

$$Pf(a) = \pi P[(4/3)\ a_{12}^3 - 2a_{12}^2 a_1 + a_{12}a_1^2 - a_1^3/6] \qquad (2\text{-}19)$$

The hydrostatic pressure, P, in equations 2-17, 18 and 19 can be replaced by the pressure from the theoretical equation of state for the scaled particle theory in which case, P, is given by

$$P = \rho kT\ [(1+y+y^2)/(1-y)^3] \qquad (2\text{-}20)$$

where ρ is the number density. For our purpose the hydrostatic pressure is used since one is interested in calculating the reversible work required to introduce a hard sphere cavity into the real fluid. The pressure contribution is virtually negligible since it contributed less than 1 cal/mole to $\bar{G}_c$. This term should only be important when conducting high pressure studies. Neglecting Pf(a) in equation 2-18 is given by

$$\bar{G}_c = RT\{-\ln(1-y) + (a_2/a_1)[3y/(1-y)] + (a_2/a_1)$$
$$[3y/(1-y)] + (a_2/a_1)^2[[3y/(1-y)] + 9/2[y/(1-y)]^2]\} \qquad (2\text{-}21)$$

The partial molar Gibbs free energy of interaction, G_i, is assumed to be given by the averaged molar interaction energy. The interaction energy between a polar solvent molecule and a nonpolar solute molecule can be described in terms of inductive, repulsive, and dispersive interactions. A Lennard-Jones (12-6) pairwise additive potential will adequately describe the dispersive and repulsive interactions while the inductive interaction energy is given by an inverse sixth power law. The total interaction energy per solute molecule is

given by

$$\varepsilon_i = C_{dis} [\Sigma_N (r_N^{-6} - \sigma_{12}^6 r_N^{-12})] - C_{ind} \Sigma_N r_N^{-6} \qquad (2\text{-}22)$$

where r_N is the distance from the center of the solute molecule to the center of the N-th solvent molecule, C_{dis} is the dispersive energy constant, C_{ind} is the inductive energy constant, and σ_{12} is the distance at which the dispersion and repulsive energies are equal in magnitude.

In order to calculate ε_i, it is assumed that the solute molecule is immersed in the solvent. The solvent is assumed to be infinite in extent and uniformly distributed around the solute molecule according to its number density. The number of molecules contained in a spherical shell a distance r from the center of the solute molecule is equal to $4\pi\rho r^2$ dr where dr is the thickness of the shell. Combining the above with equation 2-22, dividing by kT, and replacing the summation by an integration yields

$$\bar{\varepsilon}_i(d)/kT = -4\pi\rho/kT \int_d^\infty [(C_{dis} + C_{ind}) r^{-4} - C_{dis} \sigma_{12}^6 r^{-10}] dr \qquad (2\text{-}23)$$

where d is the distance from the center of the solute molecule to the center of the nearest solvent molecule. The bar over ε_i indicates that this energy is averaged over all the solvent positions and therefore is density dependent. It is this averaged energy that is assumed to be equal to the free energy of interaction. Carrying out the integration yields

$$\varepsilon_i(d')/kT = (\varepsilon^*_{dis} + \varepsilon^*_{ind}/kT)(2/d')^3 - (8/3)(\varepsilon^*_{dis}/kT)(1/d')^9 \qquad (2\text{-}24)$$

where $\varepsilon_s^*/kT = \pi\rho/6\ C_s/kT\sigma_{12}^3$ and $d' = d/r_{12}$ (2-25)

The minimum in $\bar{\varepsilon}_i(d')/kT$ occurs when d' is equal to unity and thus

$$\bar{\varepsilon}_i/kT = \bar{G}_i/kT = -5.33\ \varepsilon_{dis}^*/kT - 8.00\ \varepsilon_{ind}^*/kT \qquad (2\text{-}26)$$

In order to consider the interaction between a polar solvent molecule and polar solute molecule we can add a term to equation 2-26 to describe the dipole-dipole interaction (Keesom Force), which is also given by a sixth power law and thus

$$\bar{\varepsilon}_i/kT = \bar{G}_i/kT = -5.33\ \varepsilon_{dis}^*/kT - 8.00\ \varepsilon_{ind}^*/kT - 8.00\ \varepsilon_{ke}^*/kT \qquad (2\text{-}27)$$

The value of C_{dis} can be estimated by means of the Kirkwood-Muller formula[72]

$$C_{KM} = 6mc^2 \left[\frac{\alpha_1\alpha_2}{(\alpha_1/\chi_1) + (\alpha_2/\chi_2)} \right] \qquad (2\text{-}28)$$

where m is the mass of an electron, c is the velocity of light, α_1 and α_2 are the molecular polarizabilities of the solvent and solute, respectively, and χ_1 and χ_2 are the molecular diamagnetic susceptibilities of the solvent and solute.

The dispersive energy constant, C_{dis}, may also be evaluated in terms of the empirically determined Lennard-Jones (12-6) energy parameters using[55]

$$C_{LJ} = 4\varepsilon_{12}\sigma_{12}^6 = 4(\varepsilon_1\varepsilon_2)^{1/2}[(\sigma_1 + \sigma_2)/2]^6 \qquad (2\text{-}29)$$

where ε_1 and ε_2 are the energy parameters for the solvent and solute, respectively, and σ_1 and σ_2 are the distance parameters of the solvent and solute. Since the potential energy is rising very rapidly with decreasing distance at σ, and the values σ_1 and σ_2 are effectively equal to a_1 and a_2 respectively.

Alternately, C_{dis}, may be estimated by means of a relation developed by Slater and Kirkwood which has the formula[73]

$$\varepsilon_{dis} = (3eh/8\pi)(N\alpha^2/m)^{1/2} \qquad (2\text{-}30)$$

where e is the charge on the electron, h is Planck's constant, α is the polarizability, m is the mass of the electron, and N is the number of valence electrons.

The value of C_{ind} is given by[55,74,76]

$$C_{ind} = \mu_1^2 \alpha_2 + \mu_2^2 \alpha_1 \qquad (2\text{-}31)$$

where μ is the dipole moment and α is the polarizability and the subscripts one and two refer to solvent and solute respectively.

The value of C_{KE} is given by[74,76]

$$C_{KE} = 2\mu_1^2 \mu_2^2/3kT \qquad (2\text{-}32)$$

where μ is the dipole moment, the subscripts one and two refer to the solvent and solute respectively, k is the Boltzman constant, and T is the absolute temperature.

Substituting equations 2-29, 2-31, and 2-32 into equation 2-27 we have

$$\bar{G}_i = -(\pi\rho/6\sigma_{12}^3)\left\{5.33\left[6mc^2\left(\frac{\alpha_1\alpha_2}{\alpha_1/\chi_1 + \alpha_2/\chi_2}\right)\right] + 8.00\,[\mu_1^2\alpha_2 + \mu_2^2\alpha_1] + 8.00\,[2\mu_1^2\mu_2^2/3kT]\right\}$$

or (2-33)

$$\bar{G}_i = -(\pi\rho/6\sigma_{12}^3)\left\{5.33\,[4(\varepsilon_1\varepsilon_2)^{1/2}]\,\sigma_{12}^6 + 8.00\,[\mu_1^2\alpha_2 + \mu_2^2\alpha_1] + 8.00\,[2\mu_1^2\mu_2^2/3kT]\right\}$$

In comparing equations 2-15 and 2-33 it should be noted that a plot of ln K versus α_2 for spherical solutes (the rare gases) should give a smooth curve. Typical plots for this function for the rare gases dissolved in benzene and H_2O are shown in Figure 1. Smooth curves of this type are obtained for the solubility of the rare gases in all solvents. It has been shown that the extrapolation of this curve for spherical solutes to zero polarizability is the equivalent to determining the solubility of a hard sphere (diameter 2.55 x 10^{-8} cm) in the solvent considered[51,52,75]. This can be expressed as

$$\lim_{a_2 \to 0} \ln K = \ln K^o = \bar{G}_c/RT + \ln\,(RT/\bar{V}_1) \qquad (2\text{-}34)$$

$a_2 \to 2.55$

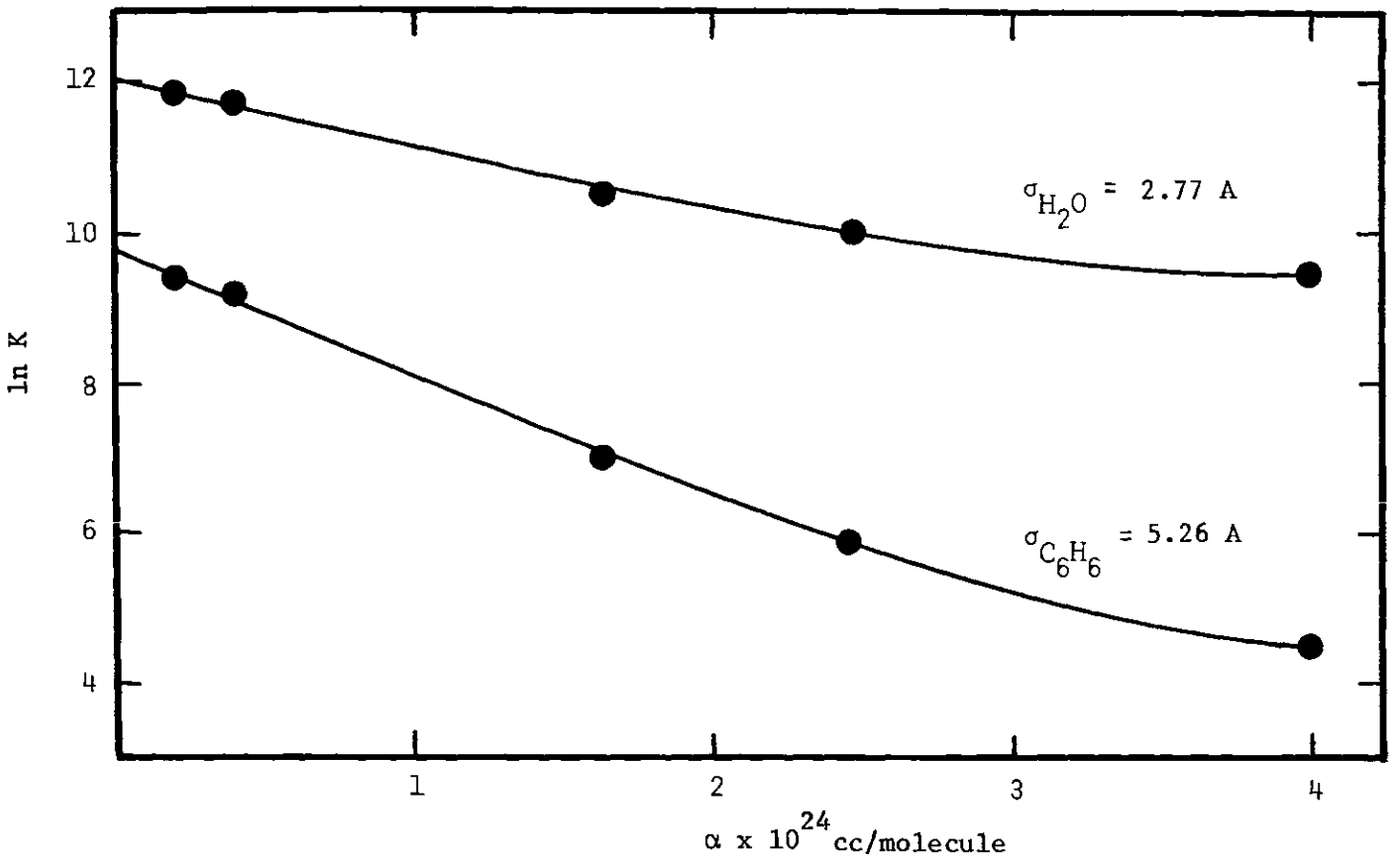


Figure 1. lnK versus Polarizability of Rare Gases in Water and Benzene at 25°C.

where K^o is the Henry's Law constant for hard spheres of diameter 2.55 x 10^{-8} cm. A plot of the variation of a_2 with respect to α_2 for the rare gases is shown in Figure 2. Extrapolation of this curve to zero polarizability gives a value a_2^o of 2.55 x 10^{-8} cm which is slightly smaller than the value of 2.58 x 10^{-8} cm obtained by Pierotti[51-53]. It is also interesting to note that a linear plot of all values of the Lennard-Jones (12-6) parameters for the rare gases, as given in Hirschfelder[55] et al., extrapolated to zero ε/k yields a value of 2.55 x 10^{-8} cm for a_2 (see Figure 3).

The value of K^o for hard spheres dissolved in a given solvent is in turn related to the "effective" hard sphere diameter of the solvent through the equations for $\bar{G}_c/kT$. Thus from the extrapolation of lnK to $\ln K^o$, the number density of the solvent ρ_1, and the temperature, the value of σ_1, the effective hard sphere diameter of the solvent, can be determined.

An alternate way of determining σ_1 from the scaled particle theory is available. Reiss et al.[41-50] have derived an expression for the heat of vaporization of a substance, yielding a value for the hard sphere size of the substance being considered.

$$\Delta H_v = RT + \alpha_p RT^2 \left[(1+2y)/(1-y)^3\right] \qquad (2\text{-}35)$$

where ΔH_v is the heat of vaporation, α_p is the coefficient of thermal expansion, and y is defined as before.

In addition to the possibility of determining effective hard sphere diameters for substances, one is also able to determine the dispersion energy parameters. It is possible to extract a value of

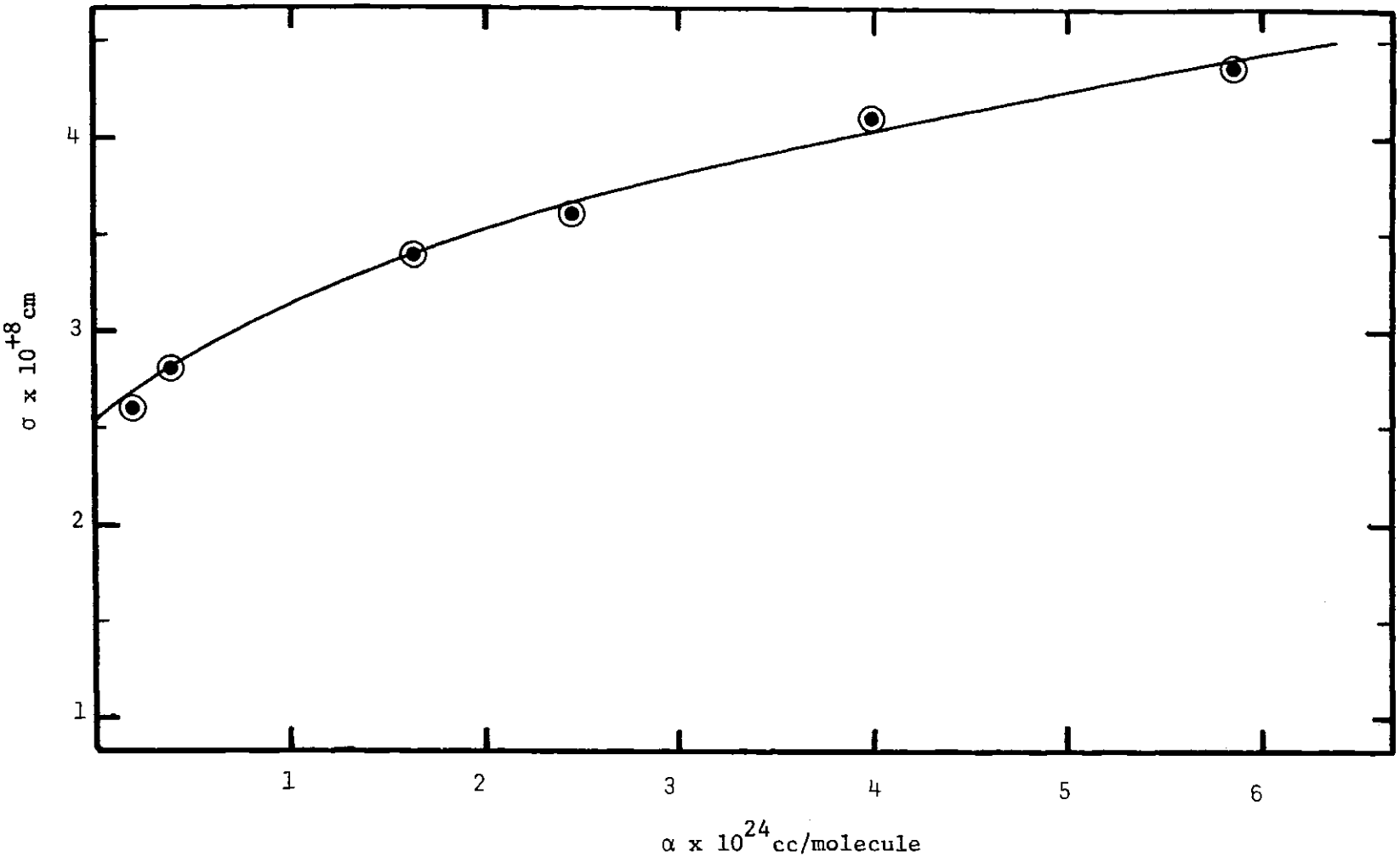


Figure 2. σ versus the Polarizability of the Rare Gases.

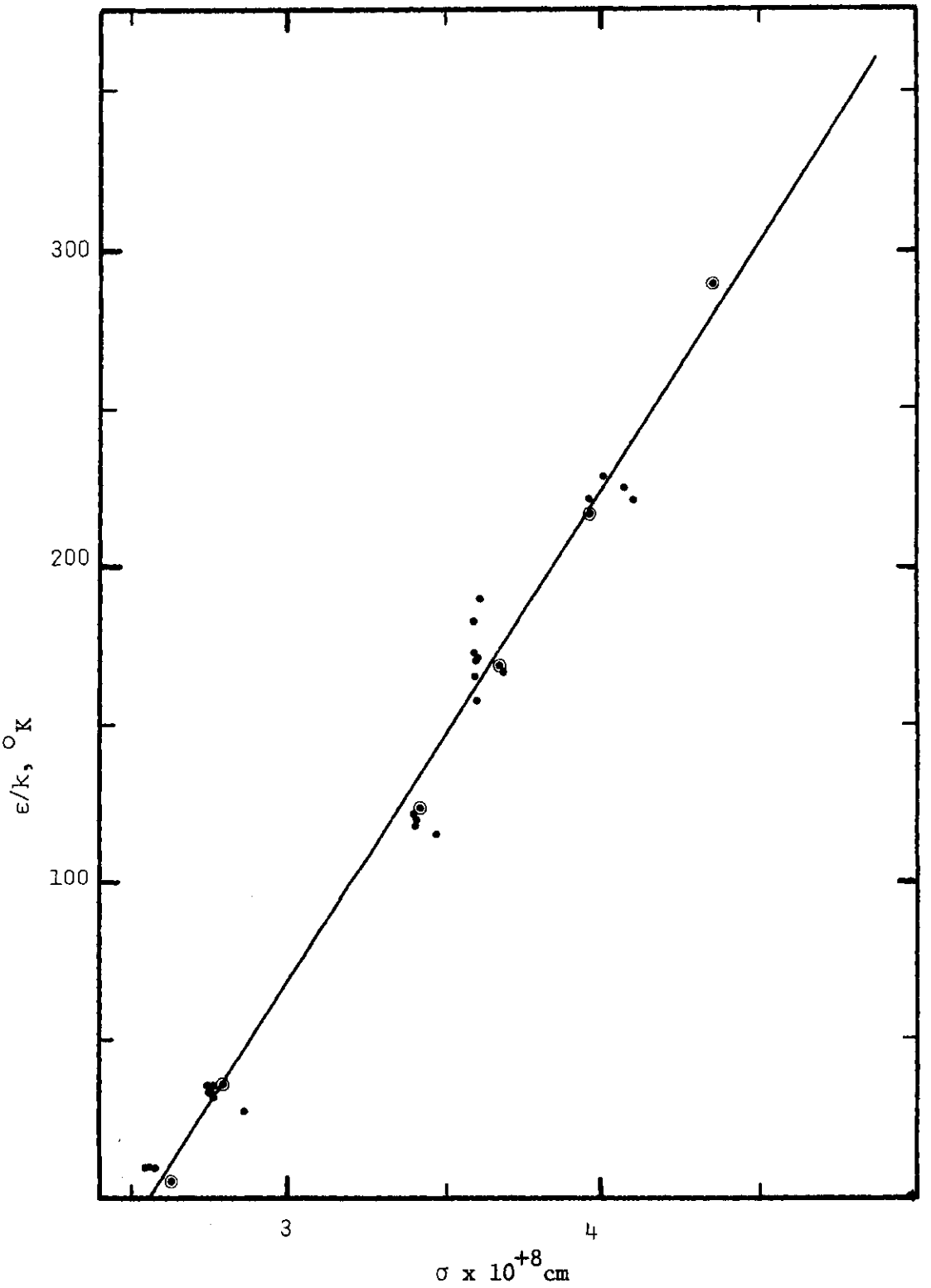


Figure 3. ε/k versus σ for the Rare Gases (◉ denotes selected values).

ε/k from the solubility of the rare gases in the solvent, because the determination of σ_1, is independent of (ε/k). Thus σ_1, can be used along with measured solubilities of the inert gases to evaluate ε^*_{dis}/kT. It is convenient to rearrange equations 2-15, 2-27, and 2-33 in the following form to calculate (ε/k).

$$\ln - 8.00(\varepsilon^*_{ind}/kT) - \bar{G}_c/kT - \ln(RT/\bar{V}_1) = - (11.17\rho_1/T)(\varepsilon_2/k)^{1/2}\sigma^3_{12} \quad (2\text{-}36)$$

The left hand side of this equation can be calculated from experimental solubilities at a given temperature along with the known physical properties of the solute and solvent and is designated as Δ. A plot of $-\Delta$ versus $(\varepsilon_2/k)^{1/2}\ \sigma^3_{12}$ should yield a straight line with slope equal to $(11.17\rho_1/T)(\varepsilon_1/k)^{1/2}$. Thus,after determining σ_1, a $-\Delta$plot can be constructed for the rare gases in the solvent and from the slope, (ε_1/k) for the solvent can be determined. A typical plot is shown in Figure 3.

The thermodynamic quantities are determined using standard techniques and in terms of partial molar quantities we have the molar free energy of solution

$$\Delta G_s = RT\ln K = \bar{G}_c + \bar{G}_i + RT\ln(RT/\bar{V}_1) \quad (2\text{-}37)$$

the partial molar heat of solution

$$\Delta H_s = [\partial \ln K/\partial(1/RT)]_p \quad (2\text{-}38)$$

the partial molar entropy of solution

$$\Delta S_s = (\partial RT\ln K/\partial T)_p = -(\partial \Delta G_s/\partial T)_p = \bar{S}_c + \bar{S}_i - R\ln(RT/\bar{V}_1) + \alpha_p RT \quad (2\text{-}39)$$

the partial molar heat capacity of solution

$$\Delta C_{p,s} = (\partial \Delta H_s/\partial T)_p = \bar{C}_c + \bar{C}_i + R(2\alpha_p T-1) + (RT^2 + T\bar{G}_i + \bar{H}_c/\alpha_p)(\partial \alpha_p/\partial T)_p \quad (2\text{-}40)$$

and the partial molar volume of the solute.

$$\bar{V}_2 = (\partial RT\ln K/\partial P)_T = (\partial \Delta G_s/\partial P)_T = \bar{V}_c + \bar{V}_i + \beta_T RT \quad (2\text{-}41)$$

The expressions for the molar quantities in terms of their contributions are given as the partial molar heat of cavity formation

$$\bar{H}_c = \alpha_p RT^2 y\ (1-y)^{-3}\ [(1-y)^2 + 3(1-y)(a_2/a_1) + 3(1+2y)(a_2/a_1)^2] \quad (2\text{-}42)$$

the partial molar heat of interaction

$$\bar{H}_i = [\partial(\bar{G}_i/T)/\partial(1/T)]_p = (1 + \alpha_p T)\bar{G}_i \quad (2\text{-}43)$$

the partial molar entropy of cavity formation

$$\bar{S}_c = -\ (\bar{G}_c - \bar{H}_c)/T \quad (2\text{-}44)$$

the partial molar entropy of interaction

$$\bar{S}_i = -(\partial \bar{G}_i/\partial T)_P = \alpha_p \bar{G}_i \quad (2\text{-}45)$$

the partial molar heat capacity of cavity formation

$$\bar{C}_c = [2/T - \alpha_p + (\partial \ln \alpha_p/\partial T)_p]\bar{H}_c - RT^2\alpha_p^2[y/(1-y)^2]^2[(1-y)^2 + 6(1-y)(a_2/a_1) + 3(10y-1)(a_2/a_1)^2] \quad (2\text{-}46)$$

the partial molar heat capacity of interaction

$$\bar{C}_i = (2 + \alpha_p T)\ \alpha_p \bar{G}_i + T\bar{G}_i\ (\partial\alpha_p/\partial T)_p \qquad (2\text{-}47)$$

the partial molar volume of cavity formation

$$\bar{V}_c = (\partial\bar{G}_c/\partial P)_T = 82.05\ (\beta T/\alpha_p)(\bar{H}_c/RT + \pi N a_2^3/6) \qquad (2\text{-}48)$$

the partial molar volume of interaction

$$\bar{V}_i = (\partial\bar{G}_i/\partial P)_T = \beta_T \bar{G}_i \qquad (2\text{-}49)$$

Solubility of Substances in H_2O and D_2O

There has been increased interest in the properties of heavy water or D_2O in recent years. This interest stems from the similarity of H_2O and D_2O, differing only in isotopic substitution of deuterium for protium. Despite the great similarity of the two substances, there are also significant differences in their physical properties as indicated in Table 1. Thus, it might be possible to elucidate the unusual properties of water in terms of molecular structure by comparing H_2O and D_2O solutions.

Let us consider the process of a gas going into solution denoted by

$$A_{gas}\ (T,f) \rightarrow A_{soln}(T,X) \qquad (2\text{-}50)$$

Table 1. Physical Properties of H_2O and D_2O.

Property	Unit	X_{H_2O}	X_{D_2O}	X_{D_2O}/X_{H_2O}
Molecular Weight	^{12}C Scale	18.015	20.028	1.117
Melting Point	^{o}C	0.00	3.81	
Temp. of max. density	^{o}C	3.98	11.23	
Molar volume at 25°C	cc/mole	18.069	18.139	1.0039
Density at 25°C[b]	gm/cc	.9970474	1.104449	1.1077
Thermal Expansion[b]	$(^{o}C)^{-1} \times 10^{5}$			
at 5°C		1.60	-11.41	
at 10°C		8.79	- 2.01	
at 15°C		15.1	6.01	
at 20°C		20.7	13.0	
Dipole moment	D	1.84	1.84	
Surface tension at 25°C	dyne/cm	71.97	71.93	0.995
Compressibility at 25°C	$(atm)^{-1} \times 10^{5}$	4.46	4.57	
Polarizability[d]	cc/molecule $\times 10^{24}$	1.47	1.46	.993
Magnetic Susceptibility[c]	cc/mole $\times 10^{6}$	-12.97	-12.76	0.985

(a) See reference 131
(b) See reference 123
(c) See reference 132
(d) See reference 125

by definition this process is the solution process, and the thermodynamic properties associated with it are the partial molar Gibbs free energy of solution

$$\Delta G_s = RT\ln K \tag{2-51}$$

the partial molar enthalpy of solution

$$\Delta H_s = [\partial(\Delta G_s/RT)\partial(1/RT)]_P = [\partial \ln K/\partial(1/RT)]_P \tag{2-52}$$

the partial molar entropy of solution

$$-\Delta S_s = (\partial \Delta G_s/\partial T)_P \tag{2-53}$$

the partial molar heat capacity of solution

$$\Delta C_{P,s} = (\partial \Delta H_s/\partial T)_P \tag{2-54}$$

the partial molar volume of solution

$$\bar{V}_2 = (\partial \Delta G_s/\partial P)_T \tag{2-55}$$

Now, a useful method of comparing the properties of H_2O and D_2O solutions is to examine the thermodynamic changes associated with the transfer of one mole of solute from an H_2O solution at unit fugacity of the solute to a D_2O solution at unit fugacity of the solute. This process is given as

$$A_{H_2O}\ (T, f_A = 1, P) = A_{D_2O}\ (T, f_A = 1, P) \tag{2-56}$$

For solutions where Henry's Law is obeyed at unit fugacity of the solute or where the Henry's Law convention is used to define the

standard state of the solute, the Gibbs free energy accompanying the process is

$$\Delta\bar{G}^{o}_{tr} = RT\ln(K_D/K_H) \tag{2-57}$$

where K_D denotes the Henry's Law constant for the solvent D_2O and K_H denotes the Henry's Law constant for the solvent H_2O. The enthalpy change associated with the transfer process is

$$\Delta\bar{H}^{o}_{tr} = RT^2[\partial\ln(K_D/K_H)/\partial T)\,]_P \tag{2-58}$$

the corresponding entropy change upon transfer is

$$-\Delta\bar{S}^{o}_{tr} = R[\partial T\ln(K_D/K_H)/\partial T]_P \tag{2-59}$$

and the corresponding heat capacity change upon transfer is

$$\Delta\bar{C}^{o}_{P,tr} = (\partial\Delta\bar{H}^{o}_{tr}/\partial T)_P \tag{2-60}$$

At this point it should be noted that the thermodynamic solution properties derived for the scaled particle theory equations 2-36 thru 2-39 are equivalent to the respective hydration properties given in equations 2-47 thru 2-50.

CHAPTER III

EXPERIMENTAL

Solubility Determinations

The saturation concentrations of pentane, cyclopentane, cyclopentene, cyclohexane, cyclohexene, 1-4-cyclohexadiene, benzene, toluene, and cycloheptatriene dissolved in H_2O and D_2O were determined using a flame ionization gas chromatograph. The two major considerations in the choice of flame ionization chromatographic analysis were the high sensitivity of the flame ionization detector and the ability of the chromatographic column to separate any impurities which have a retention time different from the material of interest.

Instrumentation and Equipment

A Varian Aerograph series 1400 gas chromatograph[77] was used in conjunction with a Hewlett-Packard Model 3370-A Electronic Digital Integrator[78]. The integrator converted the gas chromatograph analog signal into digital form precisely and automatically. The integrator measured the peak areas generated by the gas chromatographic detector and printed a number which was the area (under the peak) in micro volt-seconds, with an accuracy of 0.1 percent. A Hewlett-Packard (7100B) strip chart recorder was used to maintain visual observation of separations. Thus, the recorder served as a monitor for peak heights, widths, baseline drift, and was used as a general trouble-shooting device.

The solutions were thermalized in a constant temperature bath

equipped with a rotating basket. The rotating basket was made from a 4" x 10" x 3" metallic test tube stand. The stand was fitted with Teflon bearings which were pressed into aluminum plates. The completed assembly was sprayed with an antirust paint and mounted in the bath. A 60 r.p.m. heavy duty motor was used to rotate the basket. The temperature of the water bath was controlled using a YSI Model 71 Themistemp temperature controller which regulated the temperature to within $\pm$ 0.1^{0}C. The heating element was a 500-W metallic bar heater immersed in the water at one end of the bath. A refrigeration unit located under the bath was used to cool the entire system. A 1600 r.p.m. agitator was placed in the bath near the metallic bar heater, and was able to prevent temperature gradients in the bath within the limits $\pm$ 0.1^{o}C.

The flows[79] of the carrier and combustible gases were monitored by means of dual float (glass and stainless steel) flowmeters. The flow of each gas was initially set for minimum noise, and then final flow rates were determined by maximum sensitivity and separation of a 0.1 weight percent solution of benzene in toluene.

The chromatographic columns used were one-eighth inch stainless steel packed by Varian Aerograph Co. The column was used for all substances and was a five foot long carbowax column designated as carbowax 1540, 80-100 mesh on Chromosorb W, by Varian Aerograph Co. The column was operated at 90^{o}C for all hydrocarbons.

The miscellaneous equipment included Hamilton 7101-N 1µl syringes with chaney adaptors, 5 and 10 ml serum bottles fitted with specially designed Teflon caps. The Teflon caps for the serum bottles were tapered to fit into the serum bottles about three-fourths of an inch.

Holes were drilled to within one-eighth of an inch of the base of the cap, then threaded and fitted with an oversize brass screw. The screw, when tightened, caused the cap to expand in the bottle neck insuring effective sealing. The Teflon caps were used, because it was found that rubber stoppers absorbed hydrocarbons and that the hydrocarbons leached substances from the rubber introducing impurities into the solutions. The syringe was inserted through the hole piercing the thin portion of the Teflon at the base of the cap and the sample was withdrawn while the bottle remained in an inverted position.

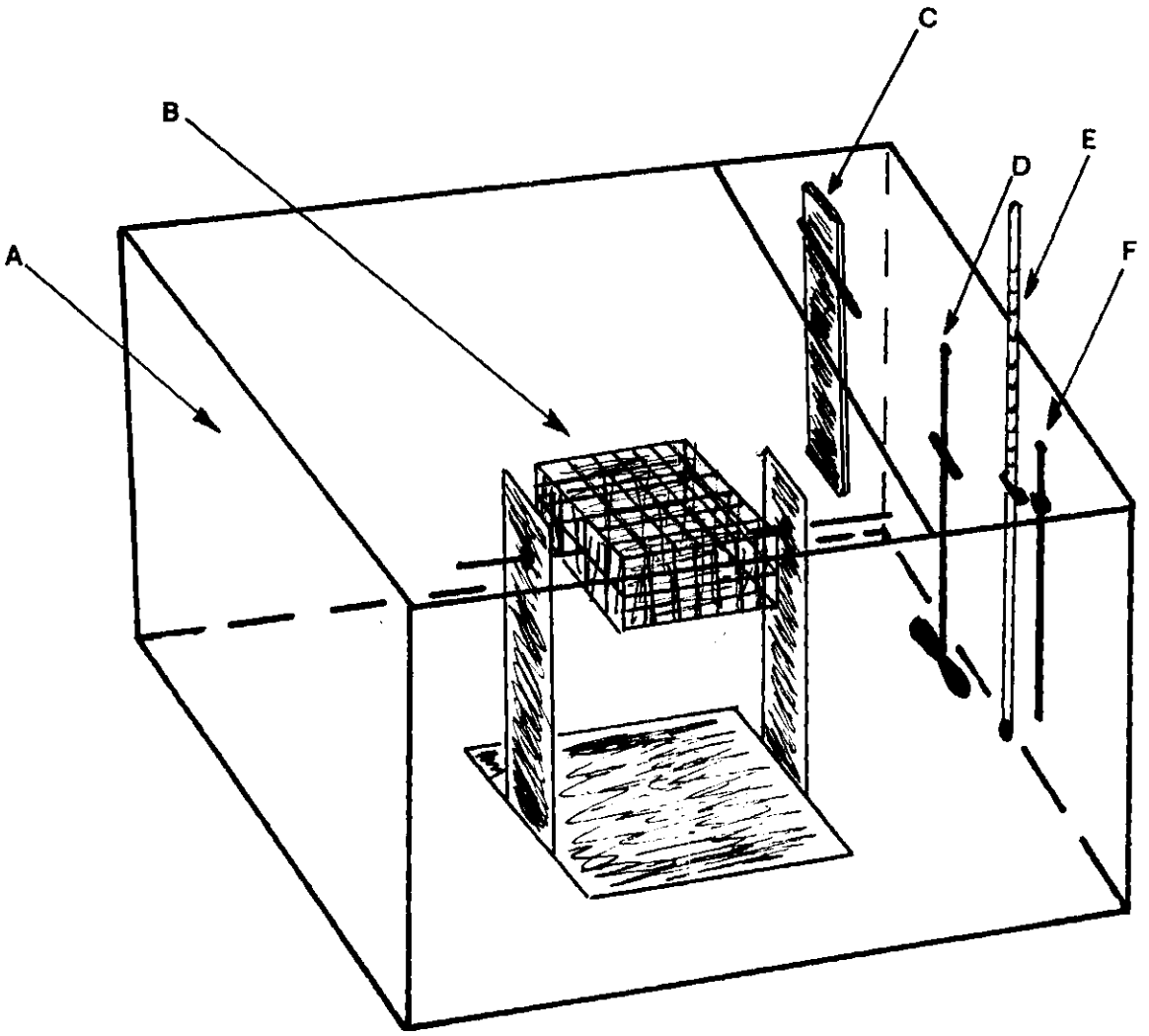
Figure 4. shows a block diagram of the experimental apparatus used in this research.

Materials

All of the reagents used in the solubility research are listed in Table 2. The commercial source, grade, and purity are also given. The reagents were used as received, except for the cyclohexene which was washed with water to remove the stabilizing agent. The purities of the reagents noted with an asterisk were determined in these laboratories utilizing gas chromatographic techniques.

The solvent D_2O used had been previously obtained from the Atomic Energy Commission of the United States and bottled at the Georgia Institute of Technology. The percentage of H_2O in the D_2O was 1.1 percent by weight, as reported in a previous investigation and also determined recently by nuclear magnetic resonance.

The solvent H_2O used was untreated laboratory distilled water, since the same solubilities were observed using either laboratory distilled or triply distilled water[80].



A - Refrigerated Bath
B - Rotating Basket
C - 500 Watt Bar Heater
D - Stirrer
E - Thermometer
F - Thermistor Probe

*The Flame Ionization Chromatograph is of standard Type (not shown)

Figure 4. Block Diagram of Constant Temperature Bath used in Solubility Determinations.

Table 2. Commercial Source, Grade, and Purity of the Reagents Used in the Solubility Determinations.

Substance	Source	Grade	Purity
pentane	Fisher Scientific Co.	Certified	Lot#794955
cyclopentane*	Matheson, Coleman & Bell	-	90.8%
cyclopentene	K and L Laboratories, Inc.	-	95-99%
cyclohexane	Fisher Scientific Co.	Certified	Lot#753122
cyclohexene	Eastman Organic Chemicals	Certified	Lot#1043
1,4-cyclohexadiene*	Columbia Organic Chemicals	-	99%
cycloheptatriene*	Columbia Organic Chemicals	Technical	83%
benzene	Matheson, Coleman & Bell	Chromatoquality	99+%
toluene	Fisher Scientific Co.	Certified	Lot#792296
hydrogen	Air Products Co.	-	-
nitrogen	Air Products Co.	Prepurified	-
air	Air Products Co.	Breathing quality	-

*Purity determined by chromatographic techniques.

Procedures

Selection of Operating Conditions. The temperature selected for column operation was 90°C, since this temperature yielded a clean separation of benzene and toluene. The optimum performance of the flame ionization detector is dependent upon the ratio of hydrogen to carrier gas flow rate[81-86], since the ratio determines the flame temperature and therefore, the efficiency of the ionization process. The optimum ratio of hydrogen to nitrogen gas flow has been determined by many investigators to be approximately equal to one. Furthermore, the flow rate of air should be such that the ratio of air to carrier gas flow is approximately equal to ten[86,87]. However, an excessive air supply may lead to turbulence in the flame zone, with resultant noise, depending upon the geometry of the detector chamber. Also, it has been shown that the optimum hydrogen-nitrogen ratio is independent of the compound type[85,88]. Using a standard calibration solution (0.7107 weight percent) of benzene in toluene the carrier gas was adjusted to obtain maximum column efficiency and then the hydrogen flow rate was adjusted to obtain maximum detector response. The operating conditions used in this research are shown in Table 3.

Calibration and Relative Ratios. A 0.7101 weight percent solution of benzene in toluene was used as the primary standard in this research. A calibration was made at least before and after each daily run. Relative ratios of response for the compounds used were determined for the pure compounds and for solutions of the compounds, of approximately one weight percent dissolved in toluene (toluene was dissolved in cumene). At this point, it was determined that the area per gram

Table 3. FID Optimum Operating Conditions

FLOW CONDITIONS	
Gas	Flow cc/min
Hydrogen	26
Nitrogen	27
Air	270

THERMAL CONDITIONS	
Section	Temperature ^{o}C
Injector Region	200
Column Region	90
Detector Region	200

responses were not the same for the neat and dilute solutions, and they also disagreed with published values.

This effect has also been observed by many other investigators[79,88-92]. The area per grams responses determined in this work for benzene and toluene as a function of concentration are shown in Figures 5 and 6. Figures 5a and 6a show the response in the dilute solution range of 0 to 15 weight percent. The area per gram response is linear with concentration over the low concentration range. Further, a plot of the response versus volume added of the 0.7107 weight percent standard solution from 0 to 1 µl was also linear. The relative ratios for the pure liquids and for the dilute (~ one weight percent) solutions are shown in Table 4, they are given relative to benzene, and are relative gram ratios. The response of the flame ionization detector remained constant throughout the period of the investigation.

Since the flame ionization efficiency is a function of the flow rates of the carrier and combustible gases, and the ionization efficiency of the referenced compounds, the response factors used were those of the dilute solutions (~ one weight percent) as they are in the same concentration range as the analyzed solutions[85].

This experiment was conducted without using a predrying column, since it was found that the calibration solution yielded a lower area per gram response with the drying column in the system.

One microliter samples of the water used in the solutions were eluted through the chromatograph and indicated no organic impurities and no change in the base line. Furthermore, during this investigation,

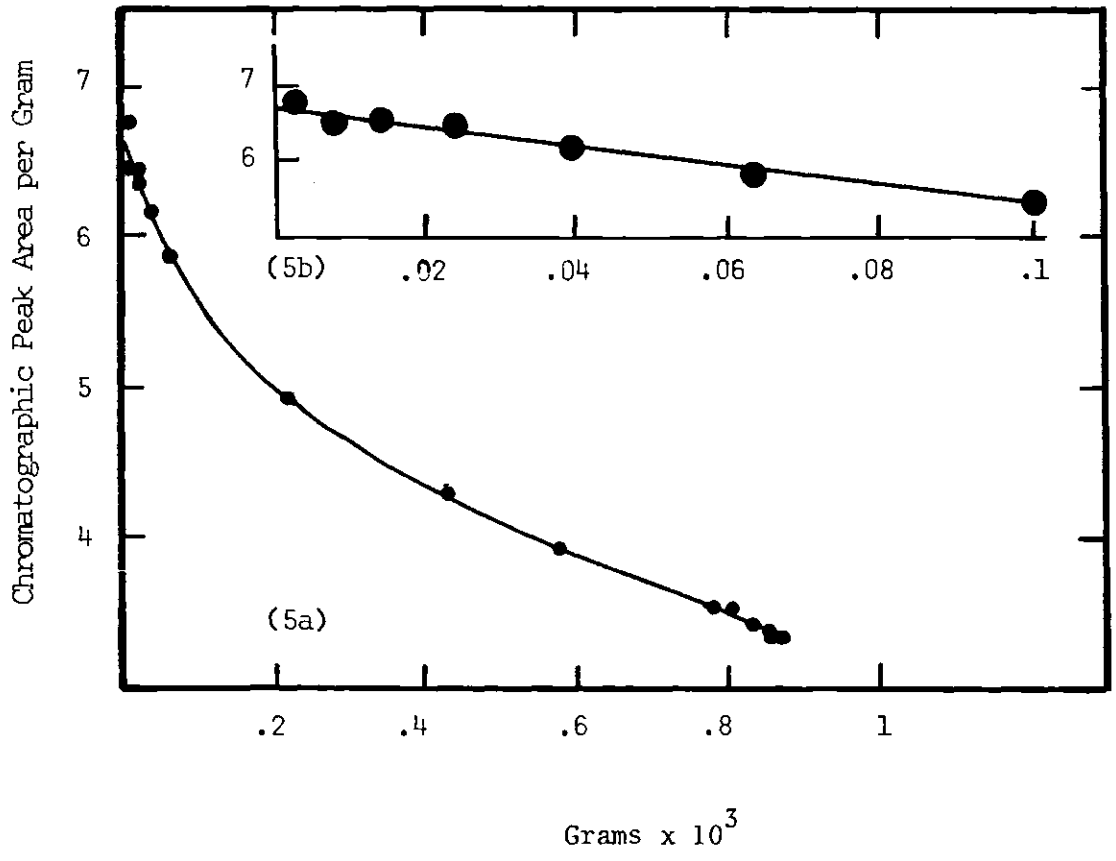


Figure 5. Area per Gram Response Factors for Benzene in Toluene.

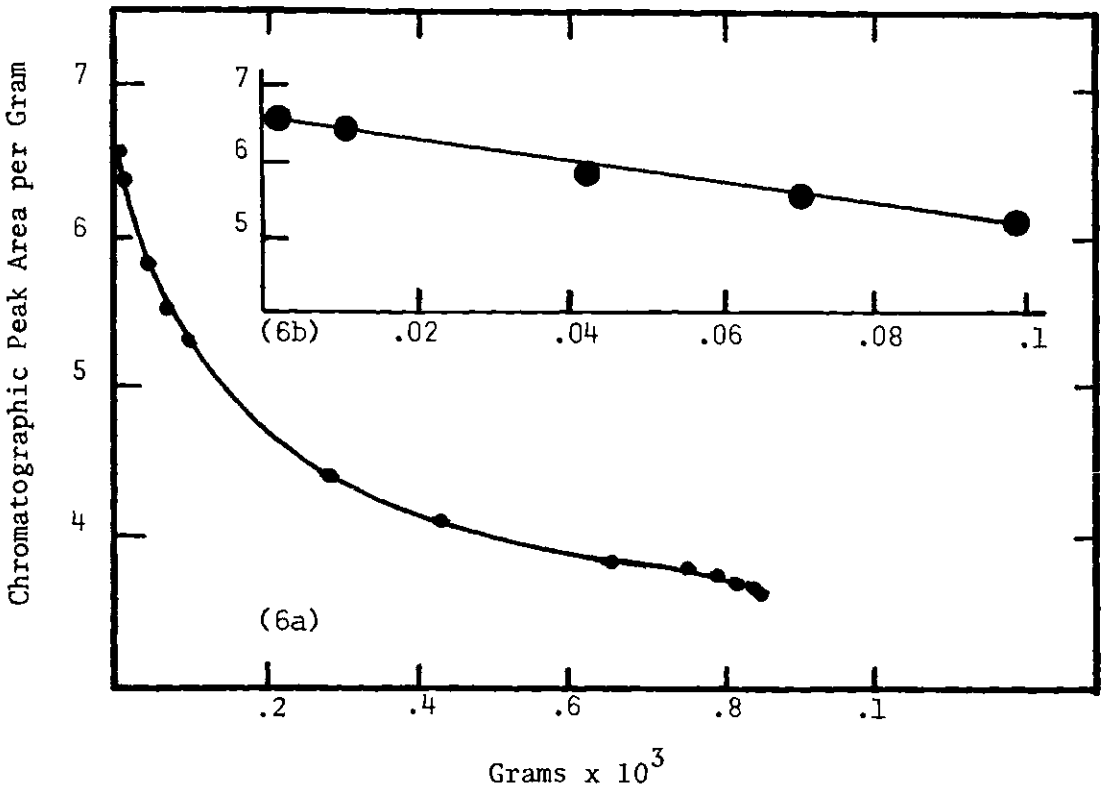


Figure 6. Area per Gram response Factors for Toluene in Benzene.

Table 4. Relative Area per Gram Ratios of Various Substances Relative to Benzene for Very Dilute and Pure Substances

Substance	Ratio 1wt%	Ratio 100wt%
n-pentane	.405	.662
cyclopentane	.527	.806
cyclopentene	.444	.803
cyclohexane	.585	.819
cyclohexene	.864	.906
1,4-cyclohexadiene	.910	1.02
toluene	1.14	1.11
cycloheptatriene	.819	.953
benzene	1	1

the base line, retention times, peak shapes, and peak heights remained constant[93-95]. The standard calibration solution yielded the same results when injected on both a dry and wet column. With respect to other previous investigations, some investigators have found that water has no effect[94-98] on the response; while others have found that water affects the sensitivity of the detector yielding various symptoms[99-103], none of which were observed by us.

This confusion surrounding the affect of water needs to be studied in greater detail as it seems to depend upon many factors, which have not yet been specifically studied with regard to how they depend upon each other. These include the geometry of the detector, amount of water injected, flow rates of gases, types of column used, injector temperature, detector temperature, and voltage used on the detector electrode.

Preparation and Sampling of the Water and Deuterium Oxide Solutions. The solutions were made by placing approximately 10 ml of solvent along with 4-10 drops of hydrocarbon in 10 ml serum bottles, which were then tightly capped and placed in the rotating basket and rotated for 24 hours. The bottles were then hand shaken to remove hydrocarbon droplets from the Teflon caps and then replaced in the bath with the tops down for an additional 24 hours.

At this point a determination was undertaken, a typical determination consisted of removing a sample bottle from the bath and injecting from 10 to 20 shots of the solution into the gas chromatograph with a 1 μl Hamilton syringe and then replacing the sample bottle in the bath and repeating the process with the next sample.

Before and after each run the calibration solution was run. The sampling was continued for a minimum of five sample runs at each temperature investigated. It was necessary to replace the column when the retention times became erratic. The chromatograph injection septa were replaced after approximately fifteen punctures.

Calculation of Weight Percent from Chromatographic Peak Areas. The peak area in a chromatographic recording is proportional to the mass of substance in the sample mixture which gives rise to the signal. In order to determine the relationship between the peak area and the mass, a calibration process is necessary. In the present study a primary calibration solution composed of benzene in toluene (0.7101 weight percent) was used. Other solute calibrations were determined relative to the benzene calibration solution by determining the relative response factors for the experimental conditions.

The calculation of the composition of an unknown solution was accomplished by determining the peak area for a given volume of solution and then taking the ratios of the peak areas and solution densities of the unknown solution and the calibration solution. Since the weight of a solution is given by

$$W = \rho V \tag{3-1}$$

where W is the weight of the solution, ρ is the density of the solution, and V is the volume of solution, it follows that from Equation 3-1,

$$W_u = [W_c (V_u/V_c) (\rho_u/\rho_c)][A_u/A_c]/F \tag{3-2}$$

where the subscripts u and c denote the unknown solution and the calibration solution respectively, A is the peak area, F is the relative area per gram ratio of substance relative to benzene and W, ρ, and V are defined as before. The factor F is introduced to compare the other solutes to the primary calibration solution which was a 0.7107 weight percent solution of benzene in toluene.

Partial Molar Volume Determinations

The partial molar volumes of solutes were determined using a high precision magnetic densimeter. The densimeter is the type constructed by Millero[104], which is simple in principle, highly accurate, and suited to obtaining the densities of solutions as a function of temperature. The densimeter used in these studies was constructed by Liotta and Hopkins[122,126].

Instrumentation and Equipment

The high precision magnetic float densimeter[104] has a sensitivity of 0.3 ppm and a precision of the order of 2 ppm. The densimeter is shown in Figure 7. which locates the major components. The solution container, A,has a volume of 110 ml and the magnet float, B, contains a magnetic core held in place with high temperature wax. The pull down solenoid, C, is used to bring the float into the field of the main solenoid. The main solenoid, D, is used to adjust the bouyancy of the float. This is accomplished by decreasing the current until the float just begins to leave the bottom of the solution container (lifts off). The component designated, E, is the support and leveling platform.

The densimeter is placed in the bottom of a constant temperature

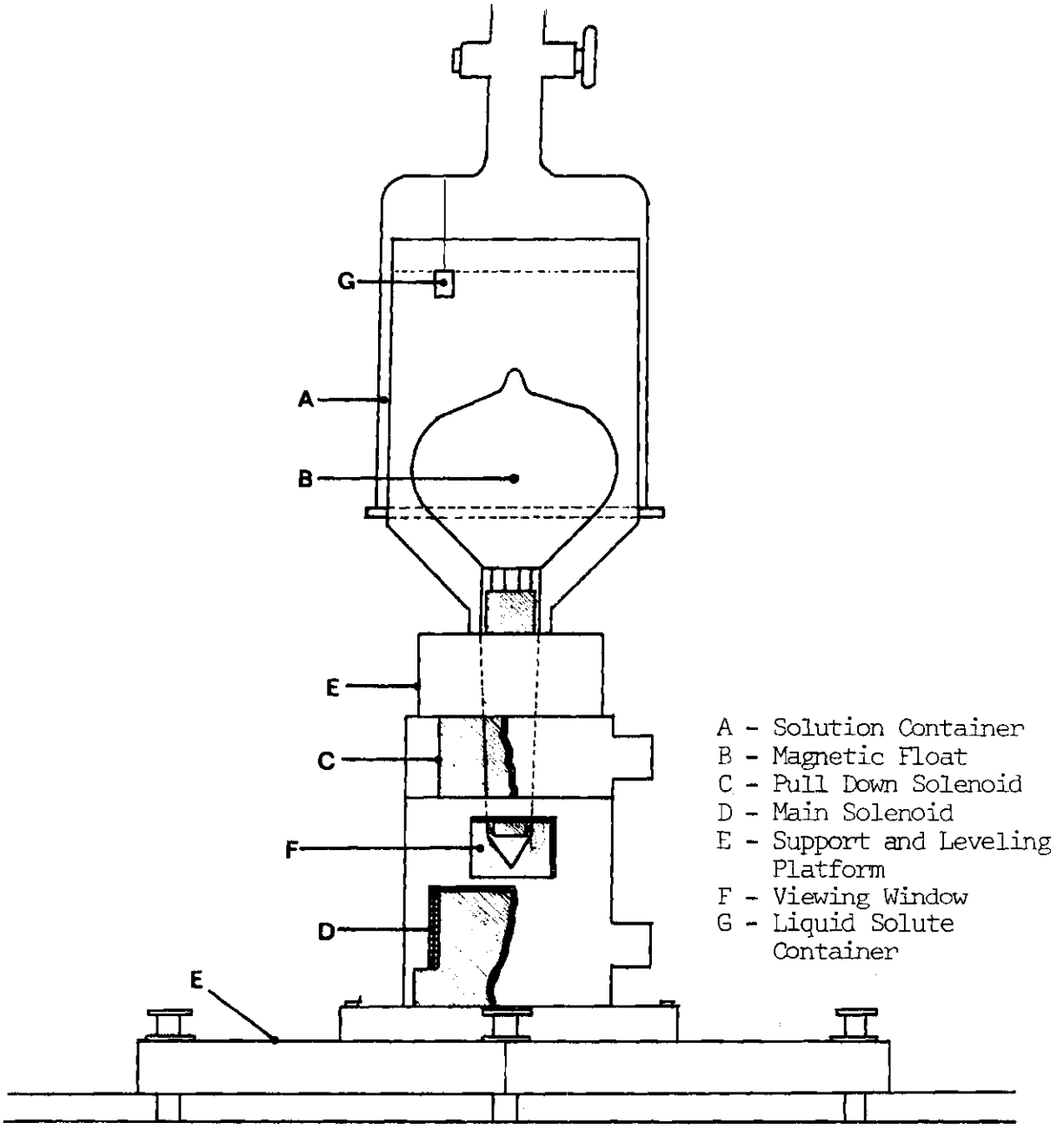


Figure 7. Diagram of the Densimeter used in the Partial Molar Volume Determinations.

bath and completely immersed in the thermalizing fluid except for the top of the stopcock on the sample container. The bath volume is approximately 30 liters and is made of Pyrex glass. The bath is enclosed in a wooden box insulated with polyurethane,and a Pyrex window was installed in one side of the box to facilitate visual observation of the float. The temperature was controlled using a PTC-1000A, precision temperature controller manufactured by Tronac, Inc., which can control the temperature to within $\pm$ 0.001°C. In order to determine the density to $\pm$ 0.0001 gm. cm^{-3} the temperature must be controlled to within $\pm$ 0.01°C due to the coefficient of thermal expansion of the solvent[105]. The temperature of the bath cycled $\pm$ 0.005°C every three to four minutes[122].

The current diagram for the apparatus is shown in Figure 8. The current passing through the main solenoid is determined by measuring the voltage across a 1.3Ω[122] standard resistor with a differential voltmeter. The voltmeter used in this work was a Hewlett-Packard 3450A multi-function meter used in conjunction with a Hewlett-Packard 5055A digital recorder. The resistance bridge used to change the current consisted of a resistance, R_1, a 0 to 10,000Ω decade (0.1Ω steps), a resistance, R_2, a 0 to 2,000Ω ten turn Borg pot and a resistance, R_3, a 0 to 100Ω ten turn Borg pot. The magnetic field of the main solenoid centers the float on the bottom and the float rotates to a fixed position. The average deviation of the hold down current is $\pm$ 3μA (corresponding to $\pm$ 0.3 x 10^{-6} gm. $cm.^{-3}$).

Materials

All of the reagents studied in the volume determination research

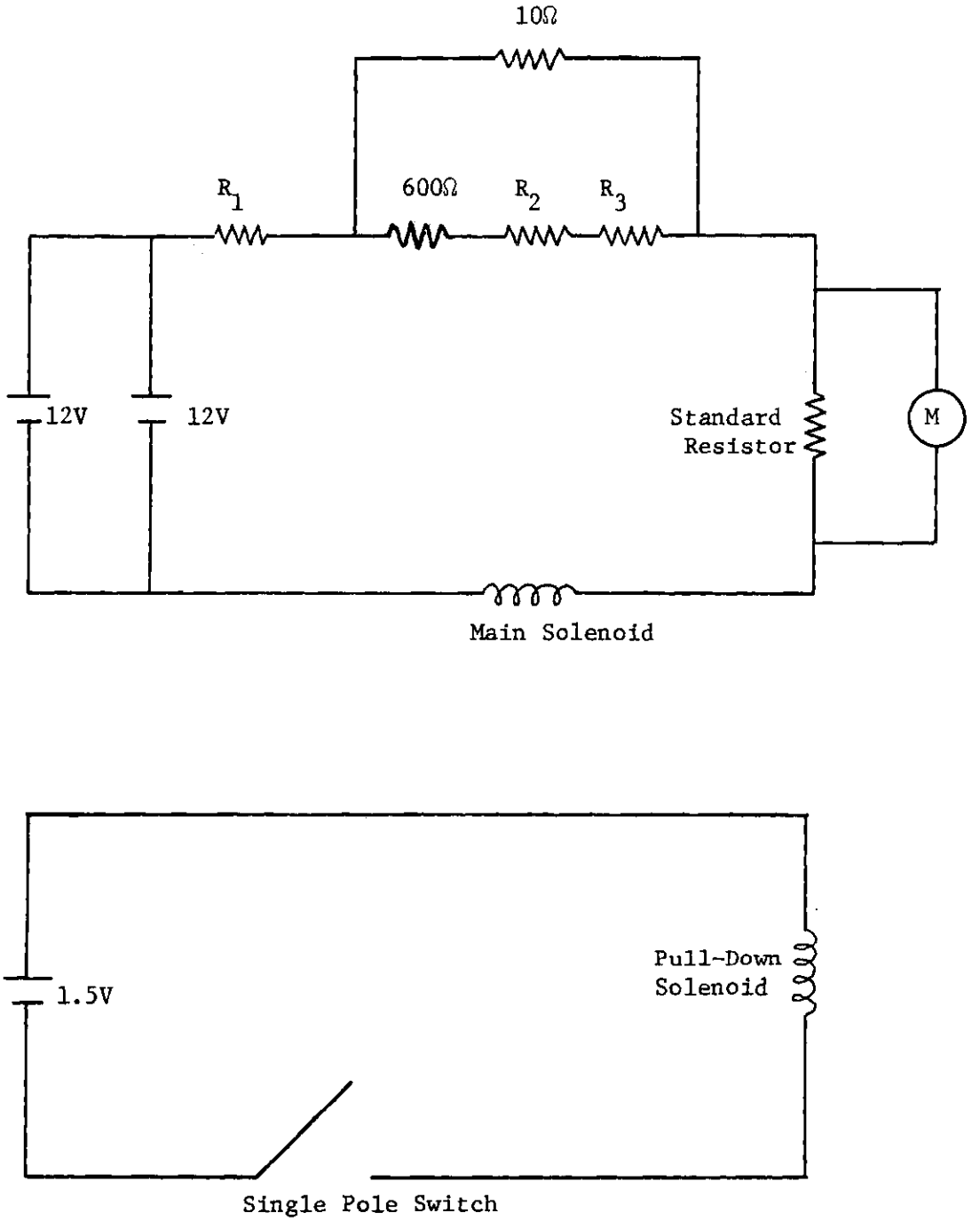


Figure 8. Current Diagram for Densimeter.

are listed in Table 5. The commercial grade, source, and melting points are given. All of the reagents used were triply sublimed under a vacuum on a cold finger.

The water used in all solutions was distilled once and then passed through a Crystallab Deemin ion exchange resin, yielding water with hardness of less than 0.4 ppm as sodium chloride. Further, the water was eluted through a flame ionization gas chromatograph which indicated no detectable organic impurities.

Procedures

All the solutions were made up by weighing (precision $\pm$ 0.1mg.). The solutions were made up at various concentrations over the concentration range 0.002m up to 0.1m. The solutions were placed in the constant temperature bath and a determination was undertaken. A typical determination consisted of measuring the density every thirty minutes for a period of three hours and then proceeding to the next sample solution. Before and after each sampling a calibration was made which consisted of determining the density of the solvent, pure water.

Table 5. Commercial Source and Melting Points after Sublimation of the Solid Reagents Used in the Partial Molar Volume Determinations.

Substances	Source	Grade	Melting Point
pyrocatechol	Fisher Scientific Co.	Practical	104.8
resorcinol	Matheson, Coleman & Bell	Resublimed	110.5
hydroquinol	Fisher Scientific Co.	Purified	174.5
pyrogallol	Baker Chemical Co.	Analyzed	130.5
phloroglucinol	Fisher Scientific Co.	Reagent	217.0
2,5-xylenol	Baker Chemical Co.	Baker	75.6
3,4-xylenol	Baker Chemical Co.	Practical	65.0
p-methyl-benzylalcohol	Aldrich Chemical Co.	-	59.8
o-cresol	Fisher Scientific Co.	Purified	31.0
t-butylphenol	Eastman Chemical Co.	Practical	99.0
p-aminoaniline	Fisher Scientific Co.	Certified	140.0
p-aminophenol	Eastman Chemical Co.	Practical	142.0

CHAPTER IV

RESULTS

Solubility Determinations

Introduction

The results of the solubility measurements in H_2O are given in Table 6. and those for D_2O are given in Table 7. and include the weight percent solubilities of the various solutes in water at temperatures ranging from 278° to $319^{\circ}K$, and the standard deviation in the measurements of a given solute at a given temperature are also given. The precision of the measurements are such that in all cases the reproducibility of the measurements are within $\pm$ 3 percent or better;with the exception of the low solubility pentane measurements,which are within $\pm$ 4 percent. Included in Tables 6.and 7.are also the mole fraction solubilities, the experimental Henry's Law constant and the calculated Henry's Law constant.

In order to calculate the thermodynamic properties of interest associated with the solution process it is necessary to determine the variation of the Henry's Law constant with temperature. Henry's Law is given by

$$f_2 = KX_2 \qquad (4\text{-}1)$$

where f_2 is the fugacity of the solute, K is the Henry's Law constant and X_2 is the mole fraction of the solute in solution. The fugacity, f, is given by

Table 6. Experimental Weight Percents, Mole Fraction Solubilities and Henry's Law Constants (Calculated vs. Experimental) of Aromatics in H_2O.

Substance	$T^{o}K$	wt%	$\pm\Sigma^{a}$	$X_2 x10^3$	$K_H^{Exp.}$ (atm)	$K_H^{Cal.*}$ (atm)
Benzene	278.16	0.2071	.0052	0.4776	96	95
	288.06	0.2078	.0055	0.4792	160	161
	293.06	0.2085	.0040	0.4809	204	206
	298.16	0.2088	.0038	0.4815	258	259
	308.26	0.2102	.0046	0.4848	400	391
	318.86	0.2300	.0054	0.5304	562	567
Toluene	278.16	0.6357	.0017	0.1243	97	98
	288.06	.06324	.0016	0.1236	175	173
	293.06	.06606	.0018	0.1292	221	227
	298.16	.06299	.0013	0.1232	303	295
	308.26	.06721	.0011	0.1314	469	478
	318.46	.06717	.0020	0.1313	748	745

*Calculated K's were calculated using the "best fit" coefficients (see Table 10).

(a) Standard deviation for weight percent solubilities.

Table 6. (Con't) Experimental Weight Percents, Mole Fraction Solubilities and Henry's Law Constants (Calculated vs. Experimental) of Alkanes in H_2O.

Substance	T^oK	wt%	$\pm\Sigma$ [a]	$X_2 x10^3$	$K_H^{Exp.}$ (atm)	K_H^{Calc*} (atm)
n-pentane	278.26	.001094	.000037	0.02732	10900	10800
	288.36	.001180	.000034	0.02946	15300	15600
	298.26	.001128	.000045	0.02816	23300	22900
	308.36	.001089	.000051	0.02719	34300	34500
cyclopentane	278.26	0.03386	.00087	0.8697	203	205
	288.36	0.03417	.00102	0.8777	314	310
	298.26	0.03419	.00067	0.8782	468	456
	308.36	0.03685	.00110	0.9465	633	663
	318.36	0.03415	.00100	0.8772	964	946
cyclohexane	278.26	.008193	.00017	.01837	2620	2590
	288.36	.008870	.00025	.01991	4050	4140
	298.26	.008884	.00024	.01998	6400	6390
	308.36	.008884	.00025	.02004	9860	9690
	318.36	.009132	.00025	.02068	14200	14300

*Calculated K's were calculated using the "best fit" coefficients (see Table 10).

(a) Standard diviation for weight percent solubilities.

Table 6. (Con't) Experimental Weight Percents, Mole Fraction Solubilities and Henry's Law Constants (Calculated vs. Experimental) of Alkenes in H_2O.

Substance	$T^{o}K$	wt%	$\pm\Sigma^{a}$	$X_2 x10^3$	K_H^{Exp} (atm)	$K_H^{Calc.*}$ (atm)
cyclopentene	298.26	0.1645	.0049	.4350	1130	1130
	308.36	0.1748	.0044	.4623	1540	1540
cyclohexene	278.26	0.02800	.00069	0.06141	707	701
	288.36	0.02985	.00061	0.06546	1120	1140
	298.26	0.02990	.00082	0.06557	1780	1770
	308.36	0.03025	.00070	0.06634	2730	2700
	318.36	0.03105	.00093	0.06809	3970	3990
1,4-cyclo-hexadiene	278.26	0.08519	.0019	0.1915	268	264
	288.36	0.09585	.0028	0.2155	385	399
	298.26	0.09362	.0023	0.2105	594	587
	308.36	0.09634	.0023	0.2166	869	855
	318.36	0.10100	.0023	0.2271	1210	1220
cycloheptat-riene	278.26	0.05809	.0014	0.1136	88	85
	288.36	0.06645	.0017	0.1299	140	143
	298.26	0.06694	.0019	0.1309	238	232
	308.36	0.07418	.0019	0.1450	357	364
	318.36	0.07648	.0022	0.1495	552	551

*Calculated K's were calculated using the "best fit" coefficients (see Table 10).

(a) Standard deviation for weight percent solubilities.

Table 7. Experimental Weight Percents, Mole Fraction Solubilities and Henry's Law Constants (Calculated vs. Experimental) of Aromatics in D_2O.

Substance	T^oK	wt%	$\pm\Sigma^a$	$X_2 x10^3$	K_H^{Exp} (atm)	$K_H^{Calc.*}$ (atm)
Benzene	278.16	0.1775	.0030	0.4548	101	101
	288.06	0.1676	.0028	0.4294	179	176
	293.06	0.1716	.0042	0.4397	223	226
	298.16	0.1712	.0045	0.4386	284	283
	308.16	0.1738	.0041	0.4453	436	428
	318.56	0.1918	.0051	0.4914	600	604
Toluene	278.16	0.05218	.0013	0.1133	107	107
	288.06	0.05135	.0013	0.1154	188	190
	293.06	0.05168	.0012	0.1123	254	250
	298.16	0.05179	.0015	0.1125	332	327
	308.26	0.05419	.0014	0.1177	523	539
	318.46	0.05185	.0017	0.1126	872	863

*Calculated K's were calculated using the "best fit" coefficients (see Table 10).

(a) Standard deviation for weight percent solubilities.

Table 7. (Con't) Experimental Percents, Mole Fraction Solubilities and Henry's Law Constants (Calculated vs. Experimental) of Alkanes in D_2O.

Substance	T^oK	wt%	$\pm\Sigma^a$	$X_2 x10^3$	K_H^{Exp} (atm)	$K_H^{Calc.*}$ (atm)
n-pentane	278.26	.001048	.000036	0.02907	10200	10200
	288.36	.001078	.000029	0.02990	15100	15100
	298.26	.001073	.000047	0.02970	22100	22000
	308.36	.001060	.000049	0.02941	31800	31800
cyclopentane	278.26	0.03192	.00060	0.9109	194	193
	288.36	0.03198	.00093	0.9126	302	306
	298.26	0.03106	.00051	0.8864	464	463
	308.36	0.03045	.00070	0.8690	690	682
	318.36	0.03071	.00091	0.8764	964	969
cyclohexane	278.26	0.008290	.00024	0.01972	2440	2430
	288.36	0.008409	.00021	0.02000	4030	4110
	298.26	0.008077	.00024	0.01921	6660	6470
	308.36	0.008735	.00025	0.02077	9510	9720
	318.36	0.008898	.00025	0.02116	13900	13800

*Calculated K's were using the "best fit" coefficients (see Table 10).

a. Standard deviation for weight percent solubilities.

Table 7.(Cont'd). Experimental Weight Percents, Mole Fraction Solubilities and Henry's Law Constants (Calculated vs Experimental) of Alkenes in D_2O.

Substance	T^oK	wt%	$\pm\Sigma$ [a]	$X_2 x10^3$	K_H^{Exp} (atm)	$K_H^{Calc.*}$ (atm)
cyclopentene	298.26	0.1441	.0041	0.4234	1160	1160
	308.36	0.1490	.0038	0.4378	1620	1620
cyclohexene	278.26	0.02502	.00064	.06096	712	705
	288.36	0.02664	.00061	.06491	1120	1150
	298.26	0.02627	.00047	.06401	1820	1790
	308.36	0.02718	.00053	.06622	2730	2730
	318.36	0.02768	.00057	.06744	4010	4020
1,4cyclohexadiene	278.26	0.07450	.0017	0.1861	276	275
	288.36	0.07984	.0023	0.1994	416	421
	298.26	0.07964	.0023	0.1989	628	618
	308.36	0.08577	.0020	0.2142	878	887
	318.36	0.08809	.0019	0.2200	1240	1240
cycloheptatriene	278.26	0.04480	.0008	0.09732	102	102
	288.36	0.05471	.0012	0.1188	153	158
	298.26	0.05729	.0012	0.1244	250	244
	308.36	0.06432	.0015	0.1397	371	385
	318.36	0.06266	.0017	0.1360	607	611

*Calculated K's were calculated using the "best fit" coefficients (see Table 10).

(a) Standard deviation for weight percent solubilities.

$$f = P + \frac{B_{2g}}{RT} P^2 + \ldots \qquad (4\text{-}2)$$

where P is the vapor pressure of the solute and B_{2g} is the second gas virial coefficient. Only terms thru P^2 were used in the present study.

The vapor pressure, P, of the solute is given by the Antoine equation as

$$\log_{10} P = A - [B/(C+t)] \qquad (4\text{-}3)$$

where A, B, and C are constants[106-108] and t is the temperature in degrees centigrade. The vapor pressure (fugacity) 1,4-cyclohexadiene was estimated by assuming the heat of vaporization to be 8100 cal/mole and using the Clausius-Clapeyron equation. (see Appendix D).

The second gas virial coefficient, B_2 is given by the Berthelot[110] equation as

$$B_{2g} = (9R/128)(T_c/P_c)\ [1-(6T_c^2/T^2)] \qquad (4\text{-}4)$$

where T_c is the critical temperature of the solute and P_c is the critical pressure of the solute[111-115].

At this point, it is useful to obtain an analytical expression for the variation of the Henry's Law constant with temperature[24,116,117]. For theoretical reasons, we tried to fit the data with an equation of the form

$$\Delta G_T^o = a + bT + cT\ \ln T + dT^2 \qquad (4\text{-}5)$$

This equation did not adequately fit the data over the entire temperature range unless additional terms in powers of T were included. These additional terms in T have a major effect on the first few derivatives

of lnK with temperature and thus this procedure is considered to be unjustifiable. In general, the best fit equation is determined by assuming no uncertainty in the data to weight the data in the fitting procedure, with the result that a more complicated expression must be used to represent the data. For instance, Franks et al.[118] found that equation 4-5 did not adequately fit their data for benzene dissolved in water as a function of temperature without the inclusion of higher powers of T. They decided to use a polynomial in T and tried increasing powers of T until they obtained a best fit and no further change in the coefficients. As a result, the fit of their experimental points is better than their data. While a second or third order polynomial would have representtd their data within the experimental uncertainty. They used the sixth order equation. A general non-empirical method of calculating thermodynamic properties from equilibrium data was tried. This method was developed by Clarke and Glew[119] and applied by Alexander et al.[116] to the solubility data of benzene in water. In this procedure the thermodynamic functions ΔG, ΔH, ΔS, and ΔC_p are considered to be continuous, well-behaved functions of temperature. The values of ΔH, and ΔC_p at some experimental temperature, T, are expressed as perturbations of their values at some reference temperature, Θ, by a Taylor's series expansion[120]. This method requires a great deal of effort[121] in order to obtain the best-fit equation and while it is rigorous, it requires very precise data measurements to justify its use over the method employed here. It was felt that the simplest equation capable of fitting the data within the experimental uncertainty would be the most desirable representation of the data.

Thus, the method used here to represent the data was to express the ΔG_T^o data as polynomial in T as

$$\Delta G_T^o = a + bT + cT^2 + \ldots \quad (4\text{-}6)$$

$$R\ \ln K = a/T + b + cT + \ldots \quad (4\text{-}7)$$

The ΔG_T^o data were fit to equations of the type above using a higher power of T until the equation represented all the data within the experimental uncertainties in the solubilities of $\pm$ 3 percent. The lowest order polynomial capable of yielding this fit was taken as representing the temperature dependence of lnK. In all cases, it was found that a second order polynomial adequately fit the experimental data. The best fit coefficients for the various solutes dissolved in H_2O and D_2O are given in Table 8.

Standard Thermodynamic Properties of Solution

The Gibbs free energy of solution is directly related to lnK by the relation

$$\Delta G_T^o = RT\ln K = RT\ln\ (P/X_2) \quad (4\text{-}8)$$

where ΔG_T^o corresponds to the transfer at temperature T of one mole of a gaseous solute at unit fugacity to a hypothetical solution at unit mole fraction having the properties of an infinitely dilute solution. Values of ΔG_T^o for the various solutes in H_2O and D_2O are given in Table 9.,evaluated at 25° C. In terms of the coefficients of polynomial which represents the data.

$$\Delta G_T^o = a + bT + cT^2 \quad (4\text{-}9)$$

Table 8. Table of Best Fit Coefficients of the Polynomial

$$\Delta G^{o}_{T} = a + bT + cT^{2}$$

Solute	Solvent	a	b	c x 10^{1}
A. Alkanes				
n-pentane	H_2O	5717.0	-41.922	1.4316
	D_2O	-3498.8	21.366	.34314
cyclopentane	H_2O	-4573.4	20.312	.24097
	D_2O	-9337.7	51.068	- .25356
B. Alkenes				
cyclopentene	H_2O	11408	-79.433	1.8495
	D_2O	6258.4	-46.838	1.3370
cyclohexene	H_2O	-7786.6	41.491	- .017443
	D_2O	-8366.6	45.373	- .081618
1,4-cyclohexadiene	H_2O	-8341.3	43.047	- .095485
	D_2O	-7365.0	36.950	.0017438
cycloheptatriene	H_2O	-9713.2	48.375	- .16721
	D_2O	2664.9	-33.456	1.1884
C. Aromatics				
benzene	H_2O	-15950	92.134	- .9255
	D_2O	-20180	120.58	-1.3971
toluene	H_2O	-12459	65.158	- .40490
	D_2O	-10159	49.132	- .11922

Table 9. Values of ΔG°, ΔH°, ΔS°, and ΔC_p° for the Various Solutes in H_2O and D_2O Evaluated at 25°, Using the Best Fit Coefficients.*

Solute	Solvent	ΔG°	ΔH°	$-\Delta S^{\circ}$	ΔCp°
A. Alkanes					
n-pentane	H_2O	5944	-7009	43.44	- 85.37
	D_2O	5922	-6549	41.83	- 20.46
cyclopentane	H_2O	3625	-6715	34.68	- 14.37
	D_2O	3634	-7084	35.95	15.12
cyclohexane	H_2O	5189	-7511	42.59	- 7.695
	D_2O	5196	-7608	42.95	46.52
B. Alkenes					
cyclopentene	H_2O	4163	-5033	30.84	-110.3
	D_2O	4179	-5627	32.89	- 79.73
cyclohexene	H_2O	4429	-7632	40.45	1.040
	D_2O	4436	-7641	40.51	4.867
1,4-cyclo-hexadiene	H_2O	3644	-7493	37.35	5.694
	D_2O	3667	-7381	37.05	- .1040
cycloheptatriene	H_2O	3223	-8227	38.40	9.971
	D_2O	3254	-7899	37.41	- 70.86
C. Aromatics					
benzene	H_2O	3292	-7722	36.94	55.19
	D_2O	3352	-7761	37.27	83.31
toluene	H_2O	3369	-8860	41.01	24.14
	D_2O	3430	-9099	42.02	7.109

*All Thermal Units are Calories.

The standard enthalpy of solution is related to the Henry's Law constant by

$$\Delta H_T^o = [\partial \ln K / \partial (1/RT)]_P \qquad (4\text{-}10)$$

The values of ΔH_T^o reported here were determined by the analytical differentation of the polynomial representation of the lnK data. In terms of the coefficients of that polynomial

$$\Delta H_T^o = a - cT^2 \qquad (4\text{-}11)$$

values of ΔH_T^o for the various solutes in H_2O and D_2O are given in Table 9., evaluated at 25°C.

The standard entropy of solution is defined as

$$-\Delta S_T^o = (\partial \Delta G_T^o / \partial T)_P \qquad (4\text{-}12)$$

The values of ΔS_T^o reported here were determined by the analytical differentation of the polynomial representation of lnK data. In terms, the coefficients of that polynomial

$$-\Delta S_T^o = b + 2cT \qquad (4\text{-}13)$$

values of ΔS_T^o for the various solutes in H_2O and D_2O are reported in Table 9., evaluated at 25°C.

The standard heat capacity of solution is defined as

$$\Delta C_{P,T}^o = (\partial \Delta H_T^o / \partial T)_P \qquad (4\text{-}14)$$

the values of $\Delta C_{P,T}^o$ reported here were obtained from the ΔH_T^o by analytical differentation of equation (4-10) yielding

$$\Delta C_{P,T}^o = 2cT \qquad (4\text{-}15)$$

values of $\Delta C^{o}_{P,T}$ for the various solutes in H_2O and D_2O are reported in Table 9.,evaluated at 25°C.

Thermodynamic Properties for Transfer

It is useful in comparing properties of H_2O and D_2O solutions to consider the thermodynamic changes associated with the transfer of one mole of solute from an H_2O to a D_2O solution under conditions of unit fugacity of solute. For this reason

$$\Delta G^{o}_{\text{transfer, T}} = (RT\ln(K_D/K_H)) \qquad (4\text{-}16)$$

values of $\Delta G^{o}_{\text{transfer}}$ were obtained by first expressing $\ln(K_D/K_H)$ as a polynomial in T. The best fit coefficients for these polynomials are given in Table 10. The values of $\Delta G^{o}_{\text{transfer}}$ at 298.15°K are given in Table 11. The values of $\Delta H^{o}_{\text{transfer}}$, $\Delta S^{o}_{\text{transfer}}$, and $\Delta C^{o}_{P\ \text{transfer}}$ were obtained from the polynomials using equations 4-10, 4-12, and 4-14, and are given in Table 11. evaluated at 298.15°K.

Data Treatment and Error Analysis

The experimental data were converted to weight percent solubilities using equation (3-2). The densities of H_2O and D_2O were taken from Eisenberg and Kauzman[123] who present the data of Kell[124]. The density of 98.8 weight percent D_2O was calculated using the formulation given by Kirshenbaum[125]

$$d = (X_1M_1 + X_2M_2)/(X_1M_1/d_1 + X_2M_2/d_2) \qquad (4\text{-}17)$$

where the subscripts one and two refer to solvent and solute respectively, X denotes the mole fraction, M denotes the molecular weight and d denotes the density.

Table 10. Table of Best Fit Coefficients of the Polynomial $\Delta G^{\circ}_{T,\ transfer} = a + bT + cT^2$

Solute	Property*	a	b	c x 10^1
A. Alkanes				
n-pentane	transfer	-9215.8	63.286	-1.0885
cyclopentane	transfer	-4764.3	30.755	- .49453
cyclohexane	transfer	-8179.2	54.565	- .90918
B. Alkenes				
cyclopentene	transfer	-5149.8	32.605	- .51255
cyclohexene	transfer	- 580.07	3.8814	-0.064175
1,4-cyclohexadiene	transfer	976.34	- 6.0970	.097229
cycloheptatriene	transfer	12378	-81.831	1.3556
C. Aromatics				
benzene	transfer	-4229.9	28.444	- .47151
toluene	transfer	2299.5	-16.025	.28568

* Transfer from H_2O to D_2O.

Table 11. Values of ΔG^{o}_{t}, ΔH^{o}_{t}, ΔS^{o}_{t}, and $\Delta C^{o}_{p,t}$ for the Transfer of the Various Solutes From H_2O and D_2O at 25°C Using the Best Fit Coefficients.*

Substance	ΔG^{o}_{t}	ΔH^{o}_{t}	$-\Delta S^{o}_{t}$	ΔC^{o}_{pt}
A. Alkanes				
n-pentane	-23.13	460.2	-1.621	64.91
cyclopentane	9.257	-368.3	1.266	29.49
cyclohexane	7.343	- 97.19	.3506	54.21
B. Alkenes				
cyclopentene	15.15	-593.6	2.042	30.56
cyclohexane	6.696	- 9.596	.05464	3.827
1,4-cyclohexadiene	22.82	112.0	- .2992	- 5.798
cycloheptatriene	30.48	327.6	- .9966	-80.83
C. Aromatics				
benzene	59.26	- 38.49	.3279	28.12
toluene	61.15	-240.0	1.010	-17.04

*All Thermal Units are Calories.

The vapor pressures were calculated using equation (4-3) where the constants of the Antoine equation are given in Appendix A. The second virial coefficients for the vapor phase were calculated using the Berthelot equation (4-4), for which the critical temperatures and pressures are given in Appendix B. In the case of cycloheptatriene the experimental virial coefficient was used[128], and for 1, 4-cyclohexadiene the vapor pressure was estimated by assuming a value for the heat of vaporization and using the Clausius-Clapeyron equation. (see Appendix D).

As referred to in Chapter III, the peak areas associated with the calibrations were essentially constant throughout the period of the investigation with an associated standard deviation of approximately one percent. The one percent standard deviation includes errors due to:dosing procedure variation, dosed volume variation, and errors associated with the ionization detection process (noise). When investigating the variation of peak area versus volume added for the calibration solution the percentage standard deviations increase as the volume added decreases. Thus,one should expect the percentage standard deviations to increase with more sparingly soluble substances, which one does observe in comparing pentane $\pm$ 4 percent to the other solutions $\pm$ 3 percent or less. It is felt that the noise level is relatively constant, and contributes more to the observed standard deviation as the amount of material dosed decreases.

The estimated error associated with the calculation of the Henry's Law constant is less than .5 percent. Neglect of the density correction for D_2O contributes approximately .1 percent to the error.

The Berthelot equation used in place of the experimental virial coefficients contributes less than .3 percent to the error.

Partial Molar Volume Determinations

Introduction

The results of the partial molar volume determinations are given in Table 12.,and include the partial molar volume at infinite dilution of the various solutes in water determined at 298.15°K and the standard deviation associated with the volume. Appendix E contains the concentration dependent volume data along with the standard deviation of the change in current.

In order to calculate the partial molar volume at infinite dilution, it is necessary to determine the variation of the apparent molal volume with concentration. The apparent molal volume is given by equation[104]

$$\phi_V = (1000/m)\ (\rho^o-\rho_s)/\rho^o\rho_s + M_2/\rho_s \qquad (4\text{-}18)$$

where m is the molal concentration, M_2 is the molecular weight of the solute, ρ^o is the density of water in gm cm^{-3} and ρ_s is the density of the solution.

The difference in density, $\rho^o - \rho_s$ is given by the equation[104]

$$\Delta\rho = f\ \Delta i/V \qquad (4\text{-}19)$$

where $\Delta\rho$ is the change in density of water due to the addition of solute, f is the weight equivalent of the float, Δi is the difference in the current needed to hold the float on the bottom, and V is the volume of the float. Once the float has been calibrated, f x V^{-1} is a constant

Table 12. The Partial Molar Volumes of Various Solute at Infinite Dilution in H_2O at 25°C Determined in This Work.

Solute	$\bar{V}_2$	$\Sigma \bar{V}_2$
1,2-dihydroxybenzene	87.08	0.17
1,3-dihydroxybenzene	88.67	0.50
1,4-dihydroxybenzene	88.90	0.23
1,2,3-trihydroxybenzene	88.53	0.22
1,3,5-trihydroxybenzene	91.77	0.16
2-methylphenol	102.10	0.04
2,5-xylenol	119.06	0.07
3,4-xylenol	118.52	0.16
4-methylbenzylalcohol	118.13	0.15
4-t-butylphenol	145.45	0.41
4-aminophenol*	94.95	0.20
4-aminoaniline	92.17	0.57
benzene*	83.60	2.42
toluene*	100.34	5.00
p-xylene*	115.80	4.66
cumene*	130.00	9.00

*Indicates only two determinations were made.

at a given temperature and equation (4-19) becomes

$$\Delta\rho = k\,\Delta i \tag{4-20}$$

The float calibration constant, k, at 25.00°C is 0.03814007 as previously determined by Abidaud, Hopkins and Liotta[126]. Substituting equation (4-20) into (4-18) the apparent molal volume ϕ_v is given by

$$\phi_v = (1000/m)(k\Delta i/\rho^o\rho_s) + M_2/\rho_s \tag{4-21}$$

$$\lim_{m \to o} \phi_v = \bar{V}_2^o = 1000k(\Delta i/m)_o(1/\rho^o)^2 + M_2/\rho^o \tag{4-22}$$

where $\bar{V}_2^o$ is the partial molar volume at infinite dilution.

When considering weak acids the apparent molar volume can be obtained from [104,127]

$$\phi_v = \bar{V}_2^o + b(1-\alpha)^2 m \tag{4-23}$$

where α is the degree of disassociation and b is a small constant. Equation (4-23) considers the apparent molar volume to be composed of contributions from the molecules and ions in solution.

Data Treatment and Error Analysis

The partial molar volumes at infinite dilution were determined by constructing plots of ϕ_v, versus m and $(\frac{\Delta i}{m})$ versus m, and fitting the data with both a linear and a quadratic regression analysis. In all the systems investigated here, the data were best fit by the linear equation. The linearity of the plots indicates that equation (4-23) is an unnecessary correction and was neglected.

The value of $(\frac{\Delta i}{m})_o$ for equation (4-22) was obtained by plotting $(\frac{\Delta i}{m})$ versus m and extrapolating to infinite dilution. A typical plot

of ϕ_v versus m and $(\frac{\Delta i}{m})$ versus m are shown in Figure 9.

The error associated with the ability to make repeated measurements on the same sample is shown in Table 12. which contains the data for all the solutes studied in this work.

Theoretical Analysis and Calculations

Determination of Effective Hard Core Diameters and Effective Interaction Parameters for Solvents

As pointed out in Chapter II, the extrapolation of the size (diameter) of the rare gas atom versus polarizability yields the effective size of a hard sphere when extrapolated to zero polarizability. In particular, if the values for the rare gases given by Pierotti[51-53] are fit with a second order polynomial and extrapolated to zero polarizability the hard sphere size generated is 2.55×10^{-8}cm (see Figure 2.) while the value obtained from a graphical extrapolation by Pierotti[51-53] was 2.58×10^{-8}cm. In comparing the values of $(\varepsilon/k)_i$ and σ_i for the rare gases given in Hirschfelder, Curtiss, and Byrd[55], one is presented with some difficulty in deciding which pair of values to use. If the $(\varepsilon/k)_i$ and σ_i pairs given in Hirschfelder, Curtiss, and Byrd[55] for the rare gases are plotted $(\varepsilon/k)_i$ versus σ_i and linearly extrapolated to zero (ε/k) using a linear regression analysis, one also obtains the hard sphere size of 2.55×10^{-8}cm (see Figure 9.). This extrapolation is similar to that proposed in Chapter II since ε/k and α are related by equations 2-29 and 2-31. This, at least allows us to select pairs of values for $(\varepsilon/k)_i$ and σ_i which are on the extrapolated line or are the closest pair to it. The selected pairs of values are given in

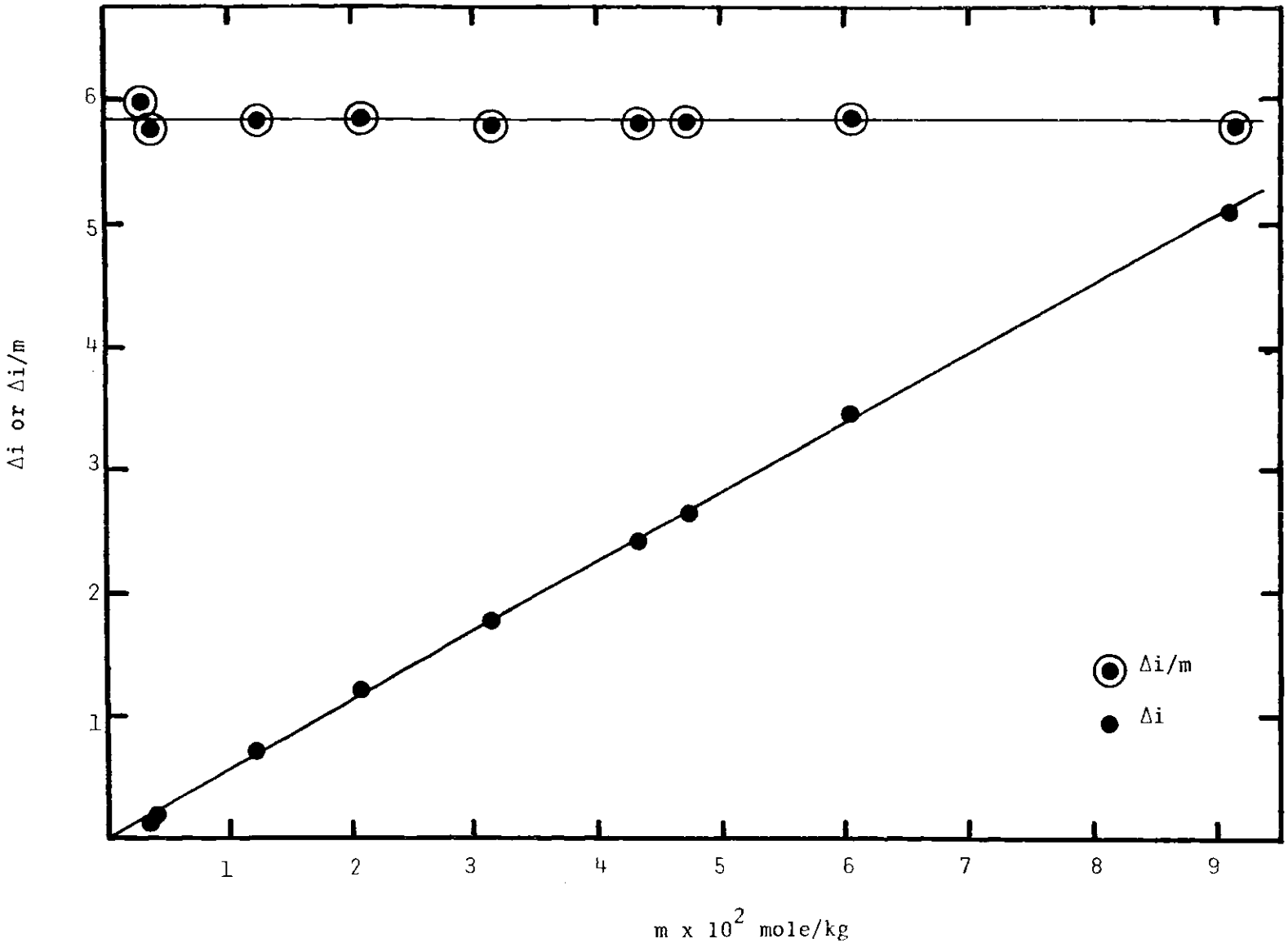


Figure 9. Plot of Δi/m and Δi Versus m for 1,3-dihydroxybenzene.

Table 13. along with values for other permanent gases.

Once the size of the hard sphere is established, the size of a substance can be determined provided the solubilities of the rare gases are known in that substance. Thus, a plot of the logarithm of the Henry's Law constant versus the polarizability extrapolated smoothly to zero polarizability yields the logarithm of the Henry's Law constant for the hard sphere, $(\ln K)_o$, dissolved in the substance under consideration. Typical plots of this type are shown in Figure 1. for the rare gases dissolved in benzene, and water. Using equation 2-15, which now becomes

$$(\ln K)_o = \bar{G}_c/RT + \ln(RT/\bar{V}_1) \qquad (4\text{-}24)$$

for a hard sphere dissolved in a substance, one can find the size (diameter) σ_1 which satisfies the equation.

The value of the solvent size, σ_1, has an uncertainty which depends upon the error associated with the solubility, the temperature, and the method or degree polynomial used in the extrapolation referred to in Figure 1. In Table 14. values are given for the sizes of various solvents determined by using both second and third order polynomials. It can be seen from the table, that in some cases, the method of fit makes no difference, while in others it can change the size by 0.03 x 10^{-8}cm. Further, it was felt that the uncertainty in the solubility data is such that a third order polynomial fit is unwarranted, and in analyzing other data a second order polynomial was used.

It was of interest to try to generate sizes for liquid alcohols; however, only limited inert gas solubility data were available. Thus,

Table 13. Values of σ, α, and ε/k for Various Permanent Gases.

Substance	σ,A	μ,D	ε/k,$^{\circ}$K	$\alpha \times 10^{24}$,cc/molecule
Helium	2.63		6.03	0.204
Neon	2.79[a]		35.7[a]	0.393
Argon	3.41[a]		125[a]	1.63
Krypton	3.67[a]		169[a]	2.46
Xenon	3.96[a]		217[a]	4.00
Radon	4.36		290	5.86
Hydrogen	2.87		29.2	0.802
Deuterium	2.87		31.1	0.775[a]
Nitrogen	3.70		95	1.76[a]
Oxygen	3.46		118	1.57
Carbon Tetrafluoride	4.70		153	2.52
Sulfur Hexafluoride	5.47[d]		260[d]	4.44[b]
Carbon Monoxide	3.76	0.13	100	1.95[a]
Nitrous Oxide	3.41[d]	0.148	114[d]	1.70
Carbon Dioxide	4.07	0.18	205	2.65[a]
Methane	3.82		137	2.60[a]
Ethane	4.42		230	4.47[a]
Ethylene	4.23		205	4.26[a]
Acetylene	4.22		185	3.33[a]

Table 13 (Cont'd). Values of σ, α, and ε/k for Various Permanent Gases.

*Unless otherwise noted, all values were taken from reference 52.

(a) See reference 55

(b) See reference 130

(c) See reference 136

(d) Average of values given reference 55.

Table 14. Values of σ and ε/k for Various Substances Acting as the Solvent

Substance	σ^a,A	σ^b,A	σ^c,A	$(\varepsilon/k)^e$,°K	$(\varepsilon/k)^f$,°K
H_2O	2.77	2.77	-	82.8	79.3
D_2O	-	2.77[d]	-	-	78.3h
n-hexane	5.98	5.94	5.87	582	543
n-heptane	6.26	6.26	6.23	663	565
n-octane	6.58	6.55	6.56	614	607[g]
n-nonane	6.85	6.84	6.86	662	659[g]
n-decane	7.12	7.10	7.12	-	695[g]
n-dodecane	7.59	7.59	7.62	815	790
n-tetradecane	8.01	8.01	8.04	-	824[g]
3-methyl-heptane	6.56	6.53	6.44	-	606[g]
2,3-dimethyl-hexane	6.54	6.51	6.80	-	606[g]
2,4-dimethyl-hexane	6.56	6.53	6.83	-	594[g]
2,2,4,-tri-methylpentane	6.57	6.53	6.48	600	584
cyclohexane	5.65	5.65	5.60	588	589

Table 14 (Cont'd). Values of σ and ε/k for Various Substances Acting as the Solvent.

Substance	σ^a,A	σ^b,A	σ^c,A	$(\varepsilon/k)^e$,^oK	$(\varepsilon/k)^f$,^oK
methylcyclo-hexane	6.01	6.01	5.98	608	613
benzene	5.26	5.26	5.25	535	496
toluene	5.65	5.65	5.68	600	573

Determined from the solubility data as described in text.

(a) fitting solubility data using 3rd order polynomial.
(b) fitting solubility data using 2nd order polynomial.
(c) determined from ΔHv using equation 2-34.
(d) determined from family of similiar curves.
(e) determined using permanent gas data.
(f) determined using inert gas data.
(g) determined using correction factor indicated in Table 16 were only He, Ne, Ar, and Kr solutions are known.
(h) determined by comparing to water using the ratio of inert slope to argon slope.
(i) selected to fit experimental data.

making it necessary to find a method of correlating the argon gas solubility data and solvent sizes (σ_1). At this juncture, it was discovered that the extrapolated solubility curves for the inert gases dissolved in similar solvents were given by a family of similar curves. Typical curves demonstrating this are shown in Figures 1, 10, 11, and 12. This relationship was used in the instances where the inert gas solubility data did not include the helium and neon data. Figure 12 shows the curves for the aliphatic alcohols, in this case, the family of curves is specified by methanol, ethanol, and isobutanol, since the solubility data for helium, neon, and argon in them is available.

As pointed out in Chapter II, equation 2-35 may also be used to generate hard sphere sizes for various substances from the heat of vaporization. However, this method of size generation should work best for non-hydrogen bonded substances. However, it has been applied to hydrogen bonding substances and yields reasonable sizes. The sizes generated in this work, using the methods described above, are shown in Tables 14. and 15.

Once the solvent sizes have been established it is desirable to determine the interaction parameters for the solvents. This is accomplished by using equation 2-34 and plotting $-\Delta$ versus $(\varepsilon_2/k)^{1/2}\ \sigma_{12}^3$ and extrapolating through the origin using a linear regression analysis. A typical plot for the solvent H_2O is shown in Figure 13. The slope of this line is proportional to $(\varepsilon/k)^{1/2}$ for the solvent. This has been done previously by using all of the permanent gas solubility data available in the substance of interest. However, it is noted that if

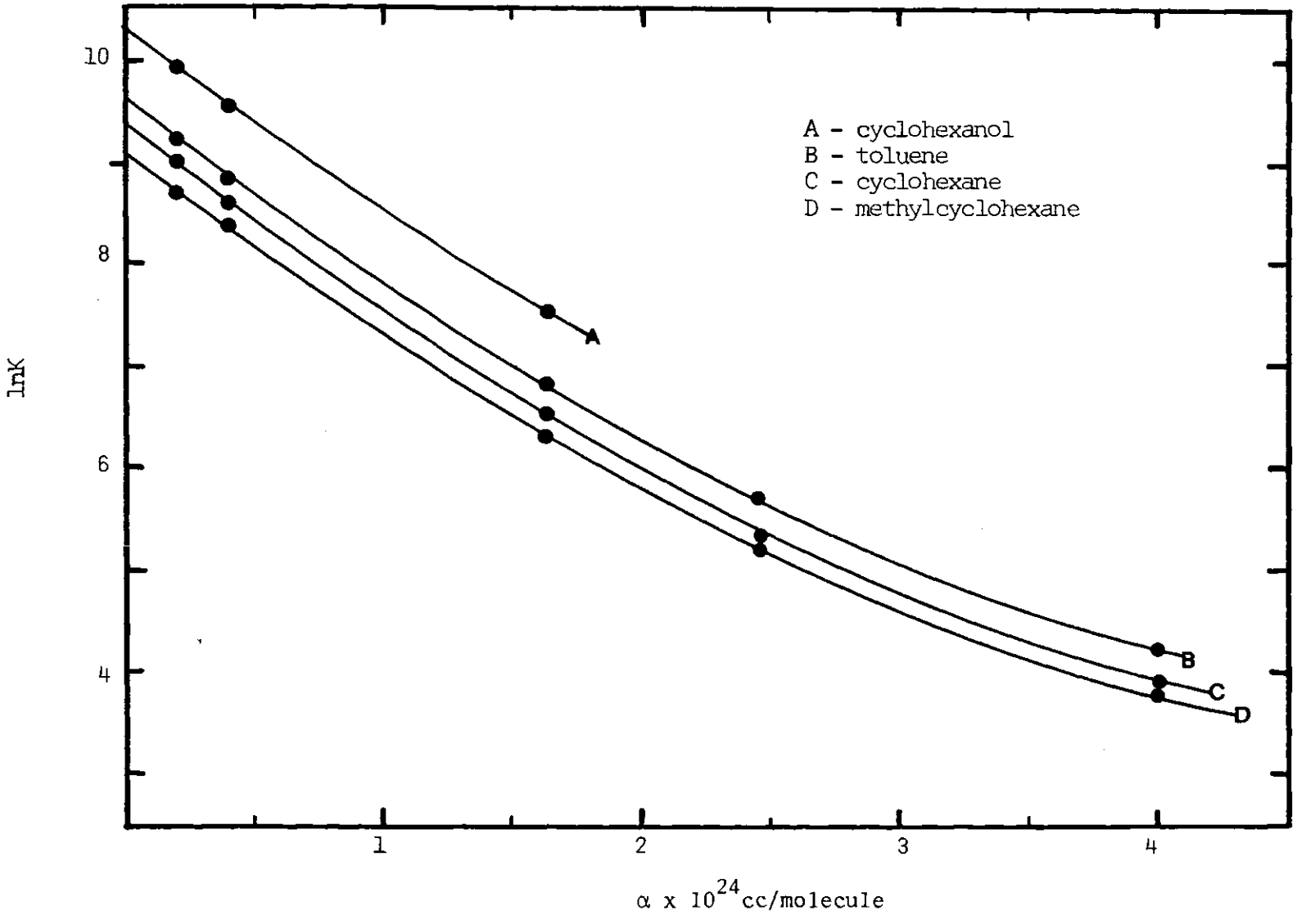


Figure 10. lnK Versus Polarizability of the Rare Gases in Various Solvents.

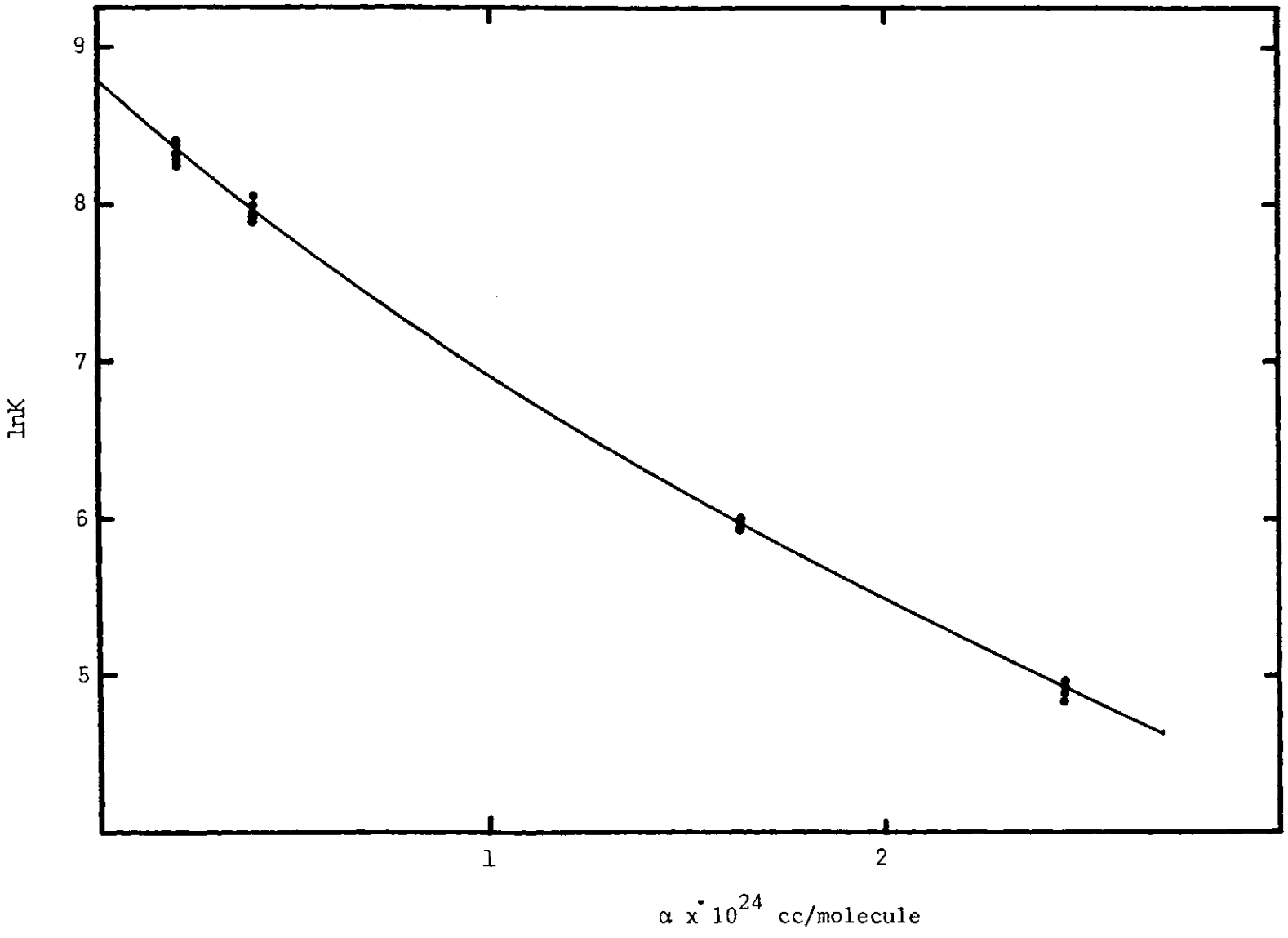


Figure 11. lnK Versus Polarizability for the Rare Gases dissolved in the n-alkanes (C_6-C_{14}).

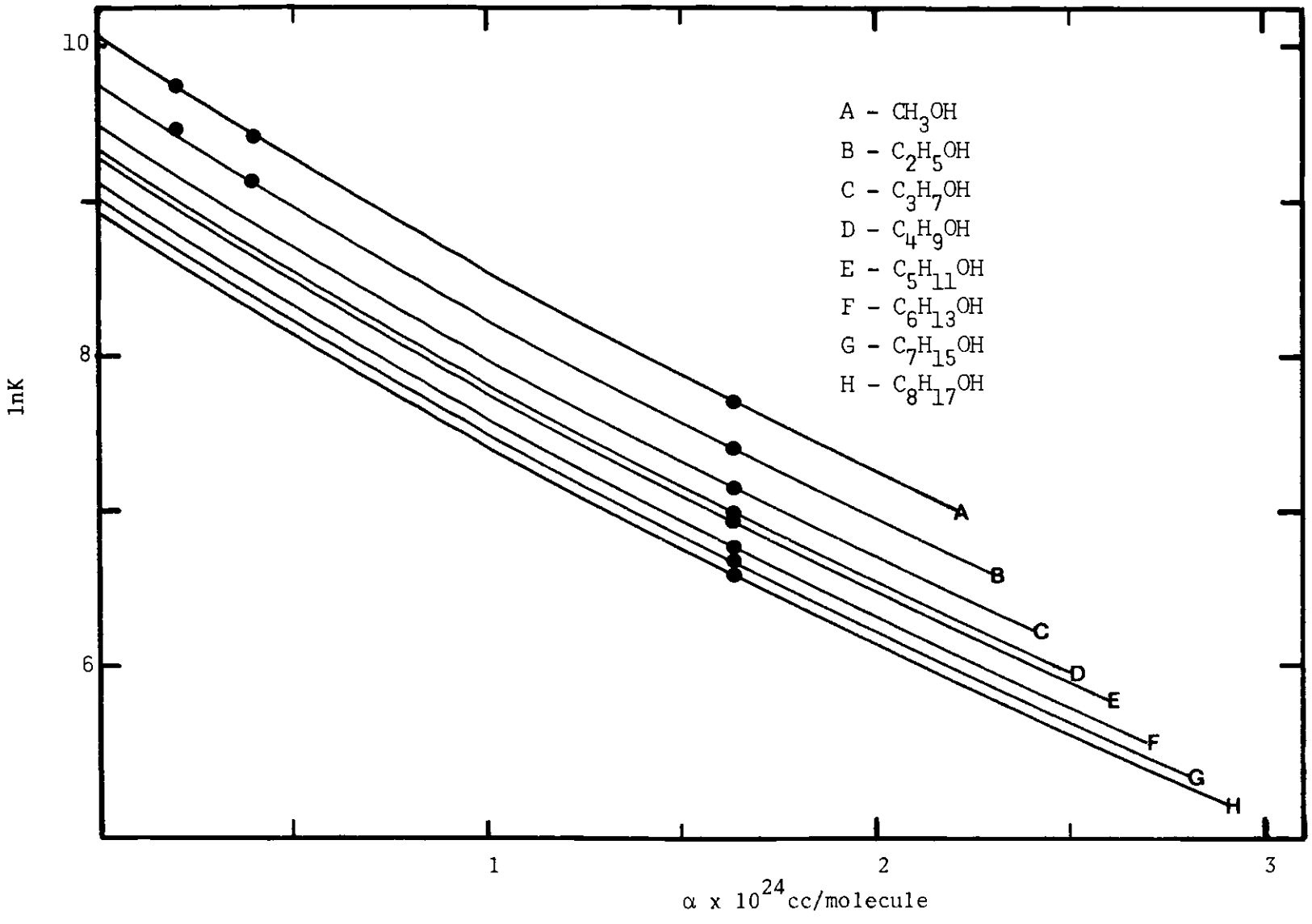


Figure 12. lnK Versus Polarizability for the Rare Gases in n-alkanols (Data from References 196 and 271).

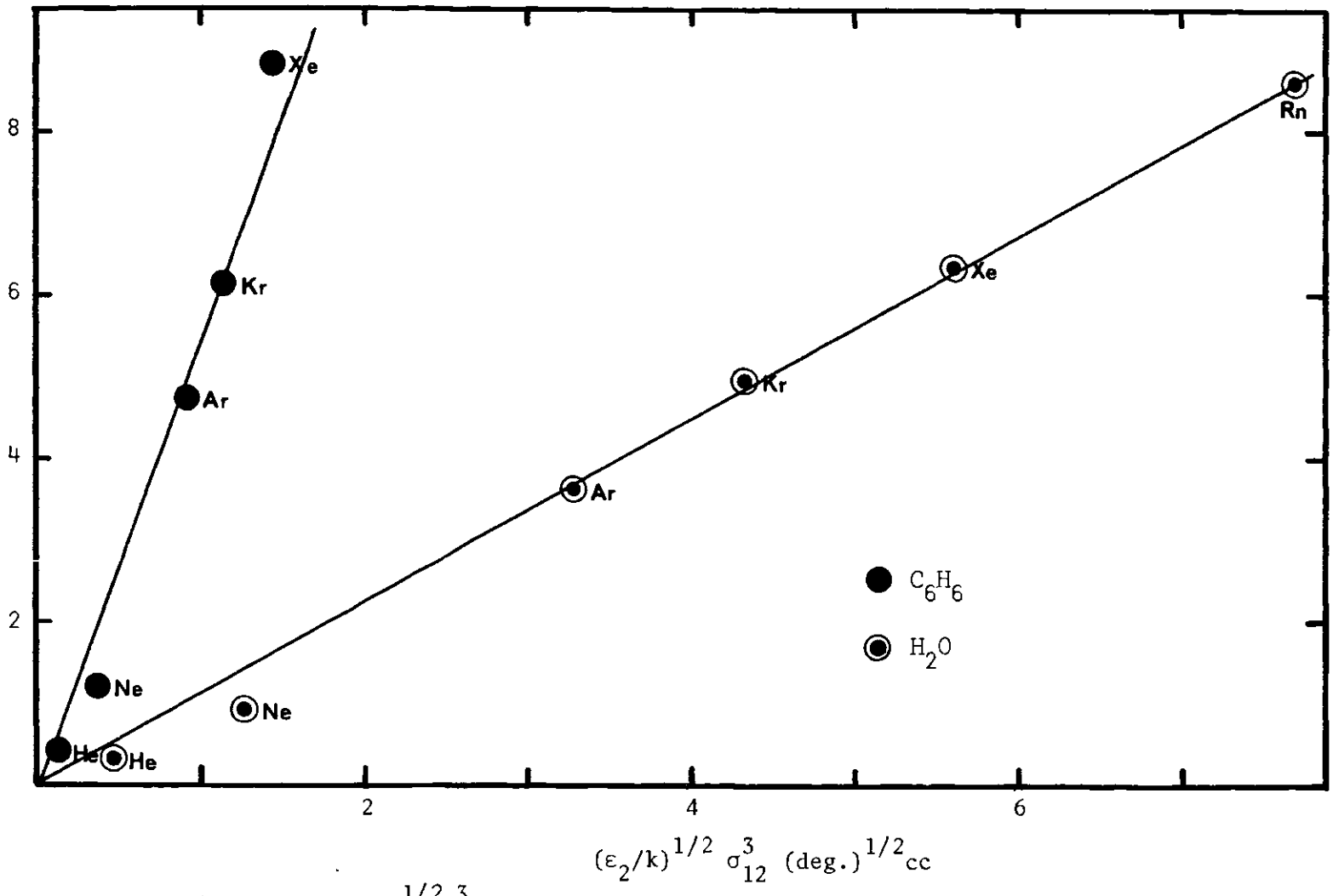


Figure 13. -Δ Versus $(\varepsilon_2/k)^{1/2}\sigma_{12}^3$ for the Rare Gases in H_2O and C_6H_6.

Table 15. Values of σ and ε/k for Various Substances Acting as the Solvent

Substance	σ^a,A	σ^b,A	$(\varepsilon/k)^c$,°K	$(\varepsilon/k)^d$,°K
methanol	3.71	4.08	260	255
ethanol	4.36	4.68	360	339
propanol	4.82	5.17	(418)	374
butanol	5.32	5.58	(462)	405
pentanol	5.62	5.93	(572)	451
hexanol	5.95	6.27	(562)	477
heptanol	6.26	6.54	(602)	506
octanol	6.54	6.86	(637)	534
isobutanol	5.30	5.58	448	471[f]
cyclohexanol	5.72	5.92	684	622
acetone	4.79	4.83	434	384
nitromethane	4.32	4.51	(320)	295[e]
carbontetra-chloride	5.38	5.35	530	530
dimethyl-sulfoxide	4.93	5.15	412	343[e]
N-methyl-acetamide	5.00	-	(411)	401
perfluoro-heptane	7.11	7.03	(495)	492
1,1,2,2-tetrachloroethane	5.60	5.761	(351)	(351)
1,1,2-trichloro-1,2,2-trifluoro-ethane	5.67	5.60	549	540
m-xylene	5.99	6.12	(660)	634

Table 15 (Cont'd). Values of σ and ε/k for Various Susbstances Acting as the Solvent.

Substance	σ^a,A°	σ^b,A°	$(\varepsilon/k)^c$,°K	$(\varepsilon/k)^d$, °K
fluorobenzene	5.31	5.33	(424)	410[e]
chlorobenzene	5.62	5.71	661	613[e]
bromobenzene	5.74	5.75	(646)	653[e]
iodobenzene	5.94	5.91	(716)	727[e]
nitrobenzene	5.75	5.83	(638)	640[e]
perfluorobenzene	5.66	5.68	555	544[f]
perfluoromethyl-cyclohexane	6.64	6.65	(429)	388
hydrazine	3.63	-	(145)	142
N-methyldrazine	4.36	-	(480)	342
N,N - dimethyl-hydrazine	4.87	-	(292)	376
perflurotri-butylamine	8.53	-	567	456[f]

Determined from solubility data as described in text.

(a) fitting solubility data using 2nd order polynomial or using family of similar curves.
(b) determined from ΔH_v using equation 2-34.
(c) determined using permanent gas data.
(d) determined using ratio factors R_2/R_4 (Tables 16 and 17).
(e) determined by using inert gas solubility data.
(f) determined using rato factor R_2/R_5 (Tables 16 and 17).
(g) brackets around values indicates few experimental solubility data available.

the slope of the line using all of the permanent gas data is compared with the slope resulting from the solubility data for the five inert gases helium, neon, argon, krypton, and xenon with ratio of these slopes agree within 2 percent.

If one considers the various pairs of $(\varepsilon/k)_i$ and σ_i data available for each permanent gas compared to the various pairs of $(\varepsilon/k)_i$ and σ_i for the rare gases, it suggests that the pair values are better determined for the rare gases. Also, by only using the rare gases, we are excluding those permanent gases which might have strong specific interactions, such as carbon monoxide, nitrous oxide, carbon dioxide, etc. These observations, together with the fact that the theoretical treatment should work best for spherical species; indicates that the best values for solvent size and interaction parameter should be obtained from the rare gas solubility in the solvent of interest.

In utilizing the rare gas solubility data for the five rare gases helium, neon, argon, krypton, and xenon, the interaction parameter for the solvent is determined. However, for most systems the solubility data of all five rare gases is not available, and neither is enough permanent gas solubility data, to adequately determine the solvent interaction parameter. The lack of adequate data necessitates the development of a correlation of the slope determined by the five rare gases to that determined by the rare gases less xenon, the argon point, and the krypton point.

The ratios for the developed correlations are shown in Tables 16., 17. and 18.; these tables include the averaged values and the standard deviations of the ratios. It should be noted that the

Table 16. The Ratios of the Slopes for the Determination of Interaction Parameters.*

Substance	R_1/R_2	R_1/R_4	R_2/R_3	R_2/R_4	R_2/R_5	R_5/R_4
benzene	1.04	1.11	1.05	1.07	1.09	-
chlorobenzene	.954	-	1.01	1.09	1.07	1.02
toluene	1.02	1.12	1.01	1.10	1.07	1.02
cyclohexane	9.99	1.09	1.00	1.09	1.07	1.02
methylcyclohexane	.996	1.09	1.00	1.09	1.07	1.02
perfluoromethyl-cyclohexane	1.05	1.10	.989	1.05	1.04	1.01
hexane	1.04	1.13	1.01	1.09	1.07	1.02
2,2,4-trimethyl-pentane	1.01	1.11	1.00	1.09	1.07	1.02
nitromethane	1.04	1.10	.990	1.06	1.08	1.01
average value	1.02	1.11	1.01	1.08	1.07	1.02
standard deviation	±0.03	±0.01	±0.02	±0.02	±0.01	±0.005

*In each case the solubility of the five inert gases, helium, neon, argon, kypton, and Xenon is known. (See Table 18 for definitions)

Table 17. The Ratios of the Slopes for the Determination of Interaction Parameters.*

Substance	R_3/R_4	R_2/R_5	R_5/R_4	R_1/R_4
octane	1.10	-	1.02	1.10
nonane	1.09	-	1.02	1.09
decane	1.09	-	1.02	-
dodecane	1.09	1.08	1.02	1.11
tetradecane	1.10	-	1.02	-
2,3-dimethylhexane	1.09	-	1.02	-
2,4-dimethylhexane	1.09	-	1.02	-
3-methylheptane	1.10	-	1.02	-
fluorobenzene	1.08	1.07	1.02	1.11
bromobenzene	1.09	1.07	1.02	1.09
iodobenzene	1.09	1.07	1.02	1.09
nitrobenzene	1.07	1.06	1.01	1.13
perfluorobenzene	1.05	-	1.01	1.09
isobutanol	1.08	-	1.02	1.07
average value	1.09	1.07	1.02	1.10
standard deviation	$\pm$0.01	$\pm$0.01	$\pm$0.004	$\pm$0.02

*In each case the xenon solubility data are unavailable.

(See Table 18 for definitions)

Table 18. The Ratios of the Slopes for the Determination of Interaction Parameters for Alcohols.

Substance	R_1/R_4
methanol	1.13
ethanol	1.12
propanol	1.05
butanol	1.14
pentanol	1.17
hexanol	1.17
heptanol	1.18
octanol	1.18
cyclohexanol	1.13
average value	1.14
standard deviation	$\pm$0.04

R_1 is the slope determined by the permanent gases.

R_2 is the slope determined by the inert gases.

R_3 is the slope determined by the krypton point.

R_4 is the slope determined by the argon point.

R_5 is the slope determined by the inert gases without Xenon.

interaction parameter is proportional to the square of the slope. The solvent interaction parameters determined in this work are shown in Tables 14 and 15.

Determination of Effective Hard Core Diameters and Effective Interaction Parameters for Solutes

The modified form of the scaled particle theory as presented in Chapter II was used to calculate the solution properties for various systems. The initial calculations indicated that the agreement between the experimental and calculated properties for the permanent gas-solvent systems was good, but the agreement was poor for larger solute-solvent systems. Further, the interaction parameter obtained for a substance acting as a solvent would not yield the correct result when that substance was acting as a solute. That is, the initial calculations indicated that the ε/k values for the larger solutes were the source of the discrepency. In fact, as pointed out by Kestner and Sinanoglu[133], interaction parameters are influenced by medium effects and further, Sinanoglu indicates that interaction parameters can decrease by as much as 40 percent in the liquid environment.

The method used to extract ε/k for the solvent (equation 2-36) uses only the rare gases as solutes and requires the solvent interaction parameters to absorb all of the perturbations, due to many body interactions and restricted rotation. At the same time, the solute interaction parameters used are the gas phase values. This suggests that a method be devised to obtain interaction parameters and sizes for molecules when they are acting as solutes, or where there are several different pairs of values for the interaction parameters and sizes are

reported for them.

The method involves selecting the molecular diameters first and is accomplished by obtaining an expression for the experimental free energy and enthalpy of solution for a given solute-solvent system in terms of the hard sphere part of the theory. This is accomplished by noting that the free energy of solution is given by equation 2-37 as

$$\Delta G_s = RT\ln K = \bar{G}_c + RT\ln (RT/\bar{V}_1) + \bar{G}_i$$

and that the enthalpy of solution is given by equation 2-38 as

$$\Delta H_s = [\partial \ln K/\partial(1/RT)]_P = \bar{H}_c + \bar{H}_i + RT\ (\alpha_p T-1)$$

and further, that $\bar{G}_i$ and $\bar{H}_i$ are related by equation 2-42

$$\bar{H}_i = (1+\alpha_p T)\ \bar{G}_i$$

combining the above in the appropriate manner yields

$$(1+\alpha_p T)\Delta G_s - \Delta H_s = (1+\alpha_p T)\bar{G}_c - \bar{H}_c + (1+\alpha_p T)[RT\ln(RT/\bar{V}_1)] - RT(\alpha_p T-1) \quad (4\text{-}25)$$

This equation allows the calculation of the solute size, and was used here to calculate the sizes of various solutes dissolved in water. Water was chosen as the solvent system, since it was felt that the experimental thermodynamic properties of water solutions are better known and most of the measurements have been done by several investigators who are in general agreement. This obviously allows one to place a higher level of confidence in the data. Table 19., lists some of the sizes for solutes generated in this way. It should be noted at this point, that the temperature appearing in the Keesom interaction is regarded as a constant throughout this work.

A general size correlation was developed by plotting the size

Table 19. Sizes for Various Solute Molecules in Solution Calculated Using Equation 4-25.

Substance	σ , A	Substance	σ , A
He	2.67	C_2H_2	2.63
Ne	2.93	C_2H_4	3.64
Ar	3.52	C_2H_6	4.33
Kr	3.72	C_2H_5OH	4.66
Xe	4.00	$C_2H_5NH_2$	4.82
Rn	4.04	C_2H_5COOH	4.25
H_2	2.77	C_3H_8	4.62
N_2	3.58	C_3H_7OH	5.30
O_2	3.63	i-C_3H_7OH	4.98
CO	3.39	$C_3H_7NH_2$	5.09
NO	3.37	C_3H_7COOH	4.60
CO_2	3.46	C_4H_{10}	5.00
N_2O	3.64	i-C_4H_{10}	4.79
COS	4.13	C_4H_9OH	5.86
CF_4	4.18	i-C_4H_9OH	5.71
CCl_4	5.25	s-C_4H_9OH	5.61
$CHCl_3$	5.12	t-C_4H_9OH	5.42
CH_3Cl	3.90	$C_4H_9NH_2$	5.39
CH_4	3.73	C_5H_{12}	5.28
CH_3OH	3.92	t-C_5H_{12}	5.56
CH_3NH_2	3.97	$C_5H_{11}OH$	6.43
CH_3COOH	3.74	t-$C_5H_{11}OH$	5.88

Table 19 (Cont'd). Sizes for Various Solute Molecules in Solution Calculated using Equation 4-25.

Substance	σ, A	Substance	σ, A
CH_3F	3.04	2,4-lutidine	5.32
CH_3Cl	3.48	3,5-lutidine	5.31
CH_3Br	3.64	pyridine	4.28
CH_3I	3.62	2-methylpyridine	4.72
C_2H_5Cl	4.10	3-methylpyridine	4.64
C_2H_5Br	4.36	4-methylpyridine	4.66
C_2H_5I	4.35	2-ethylpyridine	5.09
C_3H_7Cl	4.68	3-ethylpyridine	4.78
C_3H_7Br	4.77	4-ethylpyridine	4.61
C_3H_7I	4.77	2,3-dimethylpyridine	5.00
C_4H_9Cl	5.08	2,4-dimethylpyridine	5.14
C_4H_9Br	5.22	2,5-dimethylpyridine	5.19
C_4H_9Br	5.22	2,6-dimethylpyridine	5.40
C_5H_9Cl	5.50	3,4-dimethylpyridine	4.82
C_5H_9Br	5.62	3,5-dimethylpyridine	4.98
C_5H_9I	5.62	2-picoline	4.96
2,6-lutidine	5.53	3-picoline	4.89
2,5-lutidine	5.39	4-picoline	4.83

Table 19 (Cont'd). Sizes for Various Solute Molecules in Solution Calculated using Equation 4-25.

Substance	σ, A	Substance	σ, A
$C_5H_{11}NH_2$	5.72	piperidine	5.62
C_6H_{14}	5.33	N-methyl-piperidine	6.08
$C_6H_{13}NH_2$	6.02	di-n-propyl-amine	6.71
$(CH_3CH_2)_2O$	5.79	hexamethyl-eneimine	5.92
CH_3COCH_2	4.21	NH_3	2.78
$CH_3CH_2COOCH_3$	4.98	C_6H_6	4.33
		$C_6H_5CH_3$	4.76
CF_2HCH_2OH	4.59	$C_6H_5CH_2CH_3$	5.20
$CF_2HCF_2CH_2OH$	5.07	m-xylene	5.18
$CF_3CF_2CH_2OH$	4.82	p-xylene	5.18
$CH_3CHOHCF_3$	4.97	cumene	5.36
$CF_3CHOHCF_3$	5.43	pyrrolidine	5.33
tetrahydrofuran	4.68	N-methylpyrrolidine	5.87
2-methyl-tetrahydrofuran	5.13		
2,5-dimethyl-tetrahydrofuran	5.68		
tetrahydropyran	4.97		
1,3dioxolan	3.61		
1,4dioxolan	4.03		

versus the polarizability for the n-alkanes, where the curve was determined by the hard sphere size 2.55 x 10^{-8}cm, the methane size 3.73 x 10^{-8} cm, and the sizes for the larger alkanes, C_6-C_{14}, as given in Table 14. The result of this correlation is shown in Figure 14., which contains points for the rare gases, carbon containing permanent gases and n-alkane homologue points determined using equation 4-25. This plot indicates that the use of equation 4-25 to generate solute sizes provides a reasonable method to utilize. The equation for the size curve given in Figure 14. is given by

$$\sigma = 2.5505 + 0.54433\alpha - 0.40400 \times 10^{-1}\alpha^2 + 0.22335 + 10^{-2}\alpha^3$$
$$-0.63468 \times 10^{-4}\alpha^4 + 0.70030 \times 10^{-6}\alpha^5$$

Once the solute sizes are determined and since equation 2-34 indicates that $-\Delta$ = slope $(\varepsilon_2/k)^{1/2}(\sigma_{12}^3)$ one can solve the equation for $(\varepsilon_2/k)^{1/2}$ as the slope has been previously determined from inert gas solubility data. The solute interaction parameters determined in this way may then be plotted $(\varepsilon_2/k)^{1/2}$ versus the polarizability and the final values selected from the graph , see Figure 15. The values obtained in this way are in general agreement with those found by Kreglewski[135] derived from pseudo-critical properties.

The values for the n-alkanes, n-alcohols, and n-amines were determined in this way for the solvent water, and then used to calculate thermodynamic solution properties of these solutes in polar and non-polar solvents, and it was found that resultant calculated properties agree with the experimental properties.

It should be noted that the methods presented in this section

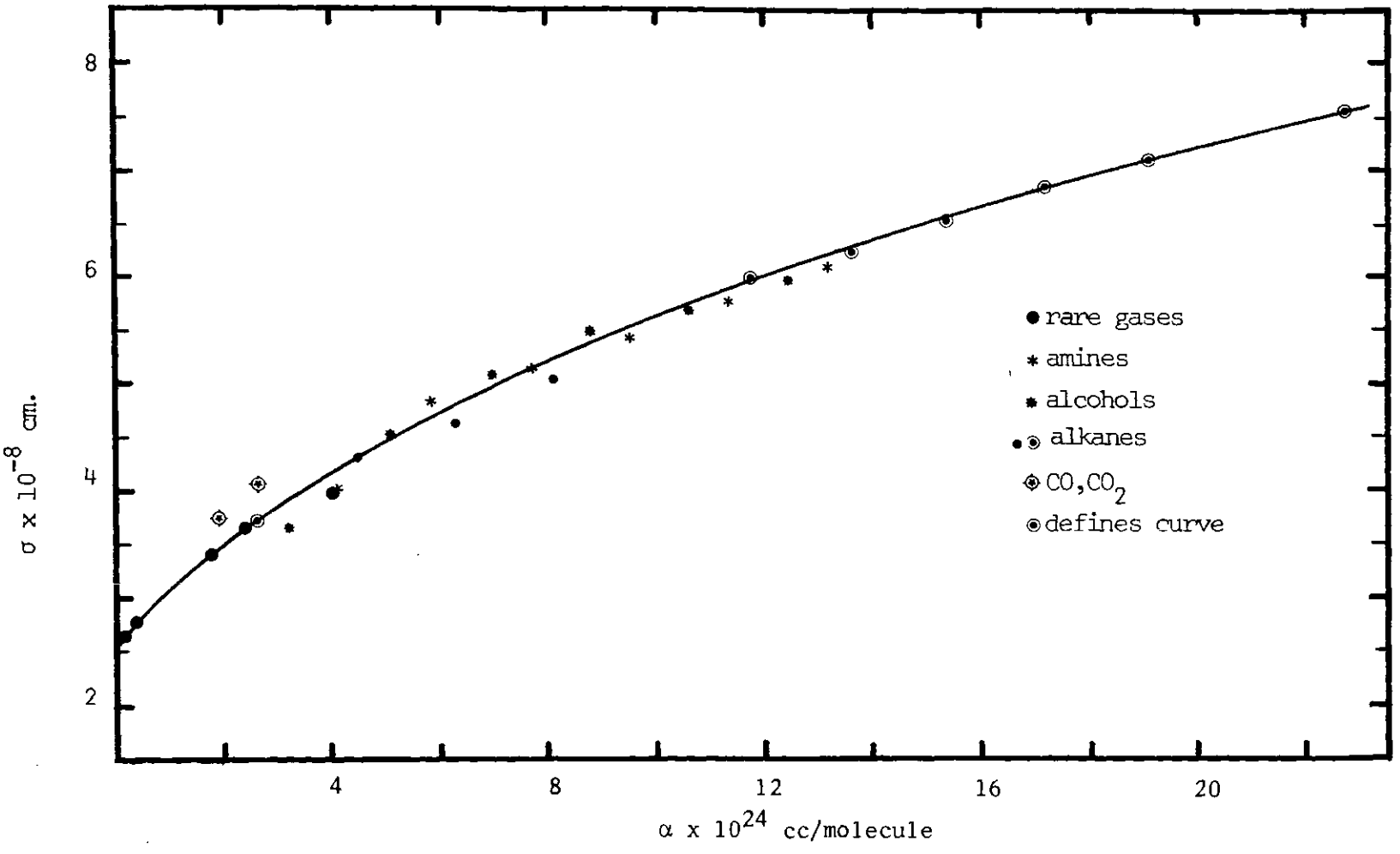


Figure 14. Molecular Diameter, σ, Versus the Polarizability.

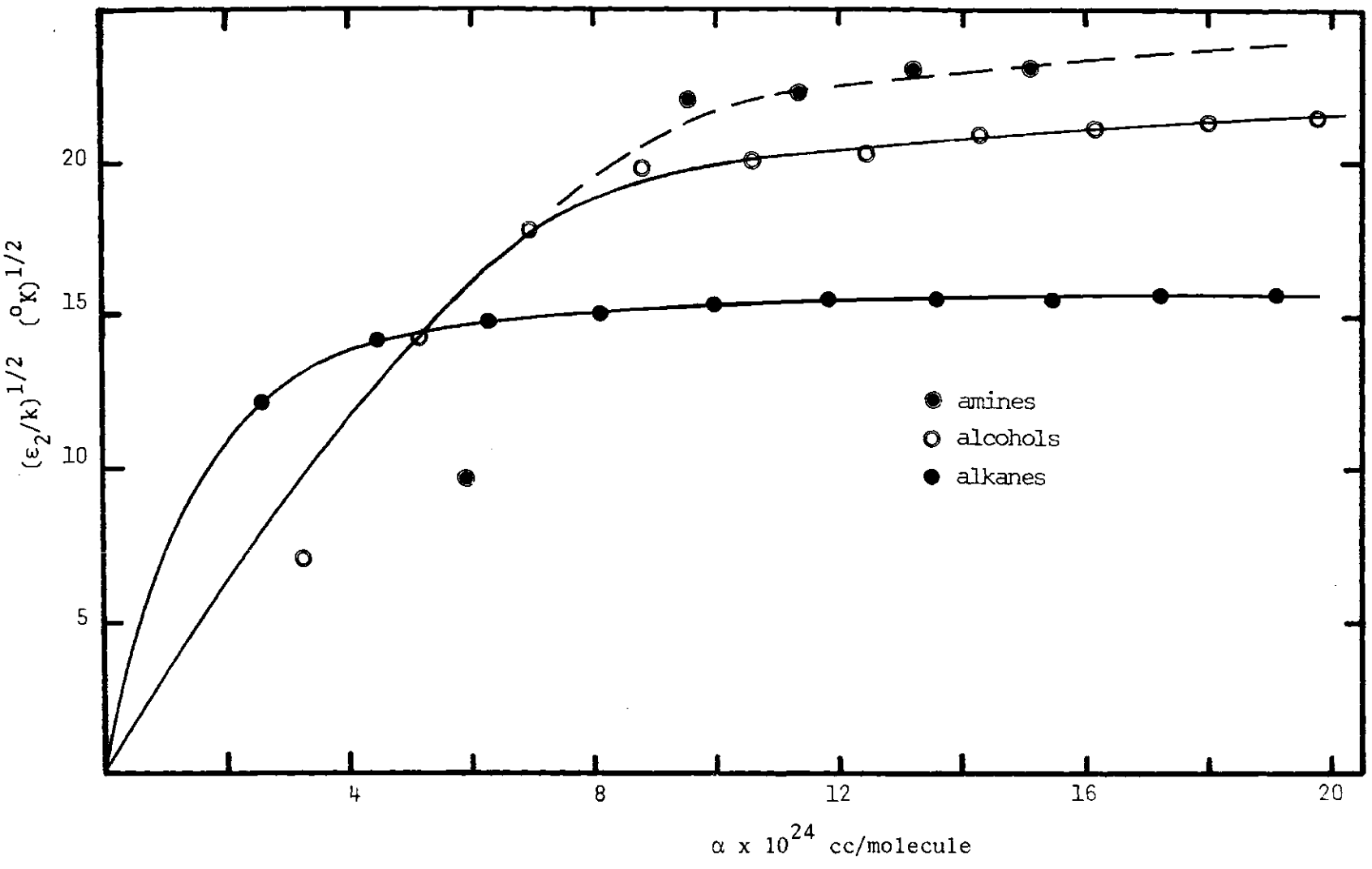


Figure 15. $(\varepsilon_2/k)^{1/2}$ Versus the Polarizability

provide reasonable and alternative ways of either obtaining solute sizes or deciding which of a group of sizes reported for a given substance would be best to use. Also, included in Figure 14. are the sizes generated using equation 4-25 for the n-alkanols and amines.

Calculation of Thermodynamic Solution Properties

Theoretical calculations were made using the modified form of the scaled particle theory as proposed. In general, the agreement between the experimental and calculated thermodynamic properties is very good. The solvents investigated included H_2O, D_2O, methanol, n-hexane, n-heptane, n-perfluoro - heptane, cyclohexane, cyclohexanol, benzene, toluene, m-xylene, chlorobenzene, carbon disulfide, carbon tetrachloride, acetone, nitrome thane, perfluorotri-n-butylamine, 1,1,2,2,-tetrachloroethane, and hydrazine for which the data is available. The systems chosen to be presented in this work include the solvents H_2O, D_2O, methanol, benzene, n-hexane, cyclohexane, and carbon tetrachloride. The results and comparisions for these calculations are contained in Appendices G and H, which contain the results for the polar and non-polar solvents, respectively. The solvent and solute physical properties used in the calculations are given in Table 20, 21, Appendix C and Appendix F.

Table 20. Solvent Parameters Used in Theoretical Calculations.

Solvent	σ^a,A	$(\varepsilon_1/k)^b$,°K	$\beta_T^c \times 10^5$ atm
H_2O	2.77	79.3	4.465
D_2O	2.77	78.3	4.587
CS_2	4.53	466	10.73
CCl_4	5.38	530	10.91
CH_3OH	3.71	255	12.58
CH_3NO_2	4.32	295	5.01[d]
CH_3COCH_3	4.79	384	12.55
nC_6H_{14}	5.94	543	16.27
nC_7H_{16}	6.26	565	14.43
nC_8H_{18}	6.55	607	12.14
nC_9H_{20}	6.84	659	11.05
$nC_{10}H_{22}$	7.10	695	10.25
$nC_{12}H_{26}$	7.59	790	9.39
$nC_{14}H_{30}$	8.01	824	8.80
C_6H_6	5.26	496	9.38
$C_6H_{15}CH_3$	5.65	573	9.40
$m\text{-}C_6H_4(CH_3)_2$	5.99	634	8.86
$c\text{-}C_6H_{12}$	5.65	589	12.3
C_6H_5Cl	5.62	613	7.61
$n\text{-}C_7F_{16}$	7.00	438	29.78[d]
$(C_4F_9)_3N$	8.53	456	-
$c\text{-}C_6H_{11}OH$	5.72	622	6.511

Table 20 (Cont'd). Solvent Parameters used in Theoretical Calculations.

Solvent	σ^a,A	$(\varepsilon_1/k)^b$,°K	$\beta_T{}^c \times 10^5$ atm
N_2H_4	3.63	142	-
1,1,2,2 tetrachloro-ethane	5.60	351	6.25

(a) Determined from rare gas solubility data.

(b) Determined from rare gas solubility or ratio method.

(c) See reference 137.

(d) Estimated by procedures given in reference 146.

(e) Selected to fit experimental solubility data.

Table 21. Solute Parameters Used in Theoretical Calculations*.

Solute	σ_2, A	ε_2/k, °K	Solute	σ_2, A	ε_2/k, °K
H_2O	2.77	200	CH_4	3.73	146
D_2O	2.77	205	C_2H_6	4.30	201
He	2.63	6.03	C_3H_8	4.80	218
Ne	2.79	35.7	C_4H_{10}	5.25	227
Ar	3.41	125	C_5H_{12}	5.63	238
Kr	3.67	169	C_6H_{14}	5.94	240
Xe	3.96	217	C_7H_{16}	6.26	241
Rn	4.23	290	C_8H_{18}	6.55	243
H_2	2.87	29.2	C_9H_{20}	6.84	245
D_2	2.87	31.1	$C_{10}H_{22}$	7.10	247
N_2	3.70	95	CH_3OH	3.98	49
O_2	3.46	118	C_2H_5OH	4.48	202
CO	3.76	100	C_3H_7OH	4.95	313
NO[a]	3.41	114	C_4H_9OH	5.38	381
CO_2	4.07	205	$C_5H_{11}OH$	5.75	403
SF_6[a]	5.47	260	$C_6H_{12}OH$	6.08	417
CF_4	4.70	153	$C_7H_{15}OH$	6.40	435
CCl_4	5.38	374	$C_8H_{17}OH$	6.68	445
N_2O	4.54	193	$C_9H_{19}OH$	6.95	455
SO_2	4.03	363	$C_{10}H_{21}OH$	7.20	465
CS_2	4.44	488	CH_3NH_2	4.18	-
H_2S	3.59	309	$C_2H_5NH_2$	4.67	94.3

Table 21 (Cont'd). Solute Parameters used in Theoretical Calculations.*

Solute	σ_2,A	ε_2/k,°K	Solute	σ_2,A	ε_2/k,°K
NH_3	2.78	-			
$C_3H_9NH_2$	5.13	-			
$C_4H_9NH_2$	5.58	495			
$C_5H_{11}NH$	5.90	510			
$C_6H_{13}NH_2$	6.28	523			
$C_7H_{15}NH_2$	6.58	531			

*Permanent gas values, see Table 13; others determined as described in Chapter IV.

(a) Average of values given in reference 55.

CHAPTER V

DISCUSSION

Solubility Determinations

The results of the solubility measurements are given in Tables 6. and 7. Plots of ΔG_T^o versus temperature are shown in Figures 17., 18., 19. and 20., and those of ΔH_T^o versus temperature are shown in Figures 21., 22., 23., and 24. Although a quadratic fit of the data was required to regenerate the experimental points to within $\pm$ 3 percent, it is clear from the figures that the free energies determined in this work,with the possible exception of the benzene and toluene results,are very nearly linear. This effect has been noted previously[129,153]. However, the distinction between being linear or almost linear is of great concern when one is interested in the derivatives of the function involved.

The most carefully studied system was the benzene water pair. This is without question the most completely studied water-hydrocarbon system reported in the literature. The weight percent solubility reported by other investigators is given in Table 22. The solubilities reported here are in general higher than those previously reported. Among the most recently reported values are those of Wordley[158], Karger[106,185], and Ben-Naim[166]. The value reported here at 25°C is 0.2088 wt percent with a standard deviation of 0.0038 for a total of 159 determinations. Thus, with the 95 percent confidence limit this result encompasses the values 0.2012 to 0.2124 weight percent. The higher values obtained in this work can not be accounted for directly.

Table 22. Comparisons of the Measured Solubility of Benzene in H_2O at 25°C.

Method of Detection	Solubility wt%	Reference
Spectrophotometric		
isopestic equilibrium	.2170	158
liquid-liquid equilibrium	.1730	118
liquid-liquid equilibrium	.1740	171
liquid-liquid equilibrium	.1790	170
liquid-liquid equilibrium	.1740	236, 237
liquid-liquid equilibrium	.1801	164
gas-liquid equilibrium	.1659	166
Chromatographic		
liquid-liquid equilibrium	.1780	234
liquid-liquid equilibrium	.2088	200
Other		
Volume uptake	.1755	238
Interferometric	.1850	239

However, extreme precautions were taken to overcome any experimental errors which might cause high values. And there are more possibilities of obtaining low values than there are of obtaining high values. This is especially true for the spectrophotometric technique. In the case of the chromatographic measurements of McAuliffe[234], there is an increasing amount of evidence that his solubility results for many hydrocarbons are low.[163,235] McAuliffe's method of using a preabsorbing column to remove the water prior to the hydrocarbon entering the chromatographic column was tried in this work and yielded low values also. In any event, it is evident that the solubility of benzene in water is not as well known as might be expected.

The temperature dependence of the benzene- water pair is in fact, very similar to that reported by others. Figure 16. shows a plot of ΔH^o_T versus temperature of previous workers[118,164,166,170,171], along with the values obtained here. All of the data were fit by the techniques described here. Table 23. shows the values of ΔH^o at 25°C determined from solubility measurements along with those determined calormetrically. It has been reported by Franks[167] that the heat should be higher than those reported from solubility measurements as is indicated by his calorimetric measurements and those of Kirshnan and Friedman[172].

The heats reported here go in the direction, but not to the extent, indicated by the calorimetric studies. Further, it is interesting to note that when the heat is separated into the vapor contribution and the solubility contribution the temperature where $\Delta H^o_{T,x_2} = 0$ for

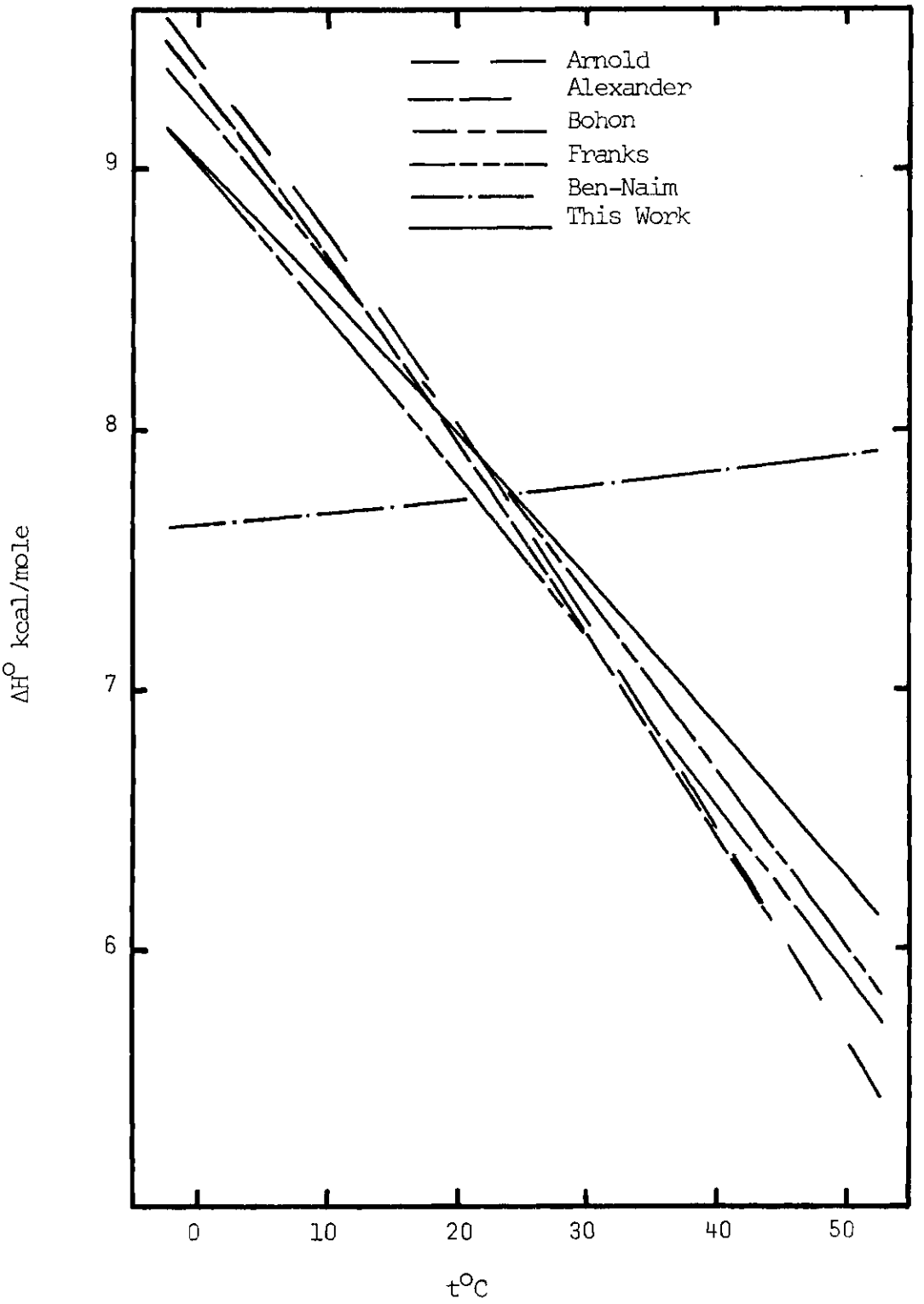


Figure 16. ΔH^o versus Temperature of Available Data. for Benzene in H_2O.

Table 23. Comparisons of ΔH_T^o for Benzene Dissolved in H_2O at 25°C.

Method	$-\Delta H_T^o$(cal/mole)	Reference
Solubility	7545	118
	7567	164
	7614	171
	7686	170
	7722	200
	7762	166
Calorimetric	7964	167
	8045	172

the various works is 289.0 $\pm$ 0.5 (see Table 23.) and that approximately 95 percent of the reported heats are contributed from the vapor phase.

The free energy of solution is given by

$$\Delta G_s = RT\ln P - RT\ln X$$

or its equivalent

$$\Delta G_s = \frac{RT}{2.303}\{A - B/(C - 273.15 + T) - 2.303(\alpha+\beta T)\}$$

where the Antoine equation is used to describe the vapor pressure and $(\alpha+\beta T)$ is used in place of ln x (since ln x is linear for most substances). Making use of the fact that $(C-273.15 + T) = \{(C - 273.15)/T + 1\}$ and that $BR/2.303\ (C-273.15)/T + 1 = (BR/2.303\ (1-C-273.15)/T + (C-273.15)/T^2 - \ldots)$ shows that over the temperature range of interest C-273.15/T is approximately a constant. Thus, ΔG_s is approximated by the analytical form finally selected to fit the experimental data obtained in this work and is given by

$$\Delta G_s = a + bT + cT^2$$

where $a = BR/2.303$, $b = AR/(2.303 - \alpha R)$ and $c = BR$

The toluene-water results are generally in very good agreement with the results of Bohon and Claussen[170]; although the values at 25°C are higher than those of other investigators. The results for n-pentane do not agree with those of Nelson and De Ligny[153], who agree within 5 percent of those of McAuliffe[234]. Both investigators used the preabsorbing column in their experimental system.

The solubilities of the remaining substances reported here

have not been studied as a function of temperature and the results reported for the solubilities in D_2O are completely new (with the exception of benzene[166]).

Standard Gibbs Free Energies of Solution

The Gibbs free energies of solution are, of course, simply related to the values of the solubility, hence the free energies for benzene calculated using the results reported here are in general, lower than those reported in the literature. The one fact that is clear is that uncertainties of $\pm$ 2 cal. are completely unjustified. Wauchope and Haque[174] carried out a statistical analysis of the work of Arnold, et al.[171] and Franks[118], et al. and conclude that at 25^0C the value of ΔG^o is 3406 $\pm$ 2 cal/mole. The uncertainty in the experimental measurements of these workers is such as to place an uncertainty of $\pm$ 20 cal./mole in ΔG^o. In addition, the values of the solubilities reported here would give a value of $\Delta G^o_{25^oC}$ of 3295 $\pm$ 20 cal./mole. Hence, the absolute value of ΔG^o may well be in question to the amount of 100 or more cal./mole.

The results for toluene in H_2O are in considerably better agreement with that reported by Wauchope and Haque[174], using the data of Bohon and Claussen[170]. They report $\Delta G^o_{25^oC}$ of 3389.9 $\pm$.7 cal./mole, while the result reported here is 3387 $\pm$ 20 cal./mole. An uncertainty of 0.7 cal./mole is completely unrealistic when considering measurements with the large uncertainties associated with the determination of these low solubility substances.

The results for ΔG^o_T for the other substances have not been previously reported.

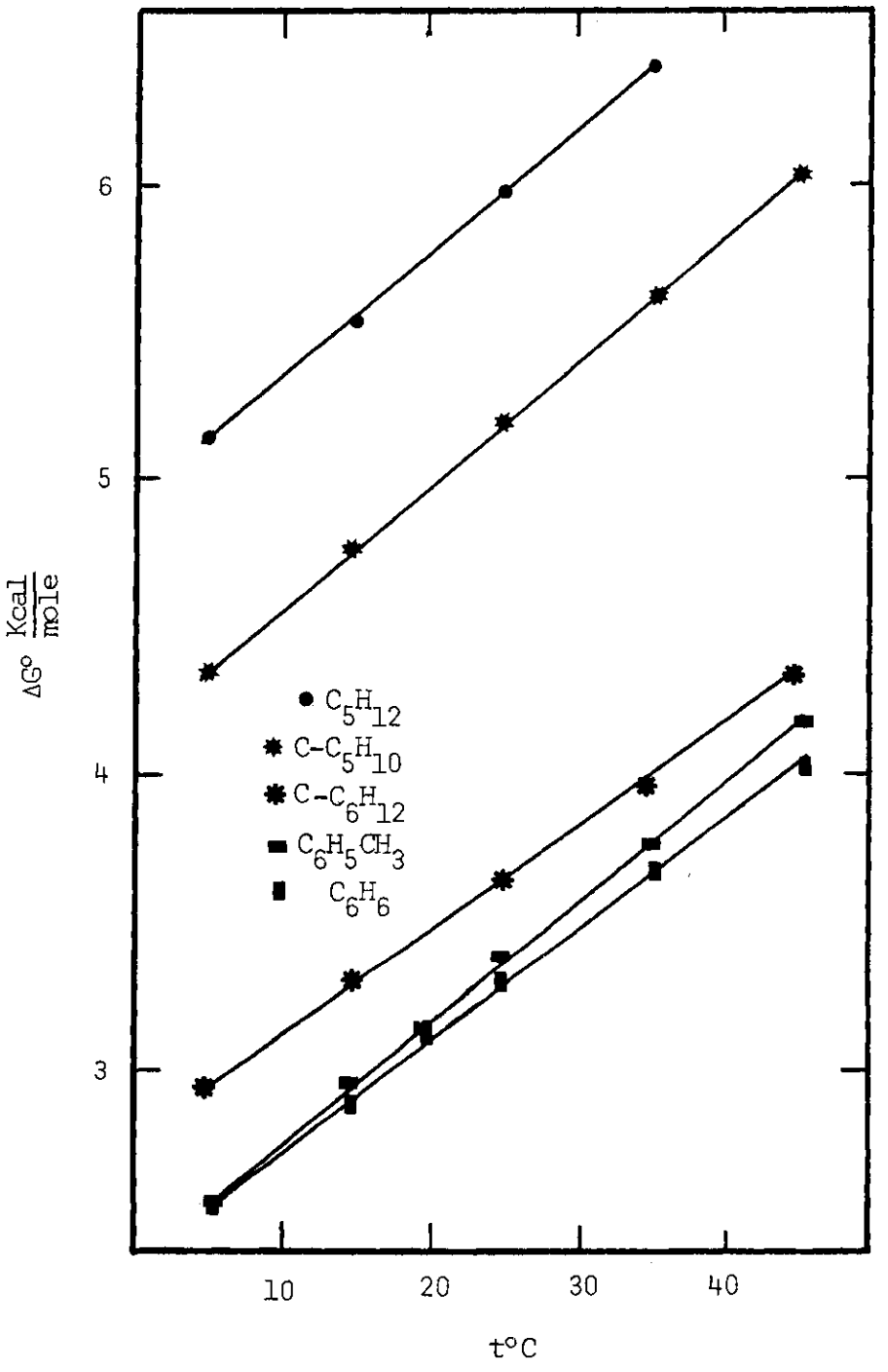


Figure 17. ΔG° for Solutes in H_2O as a Function of Temperature.

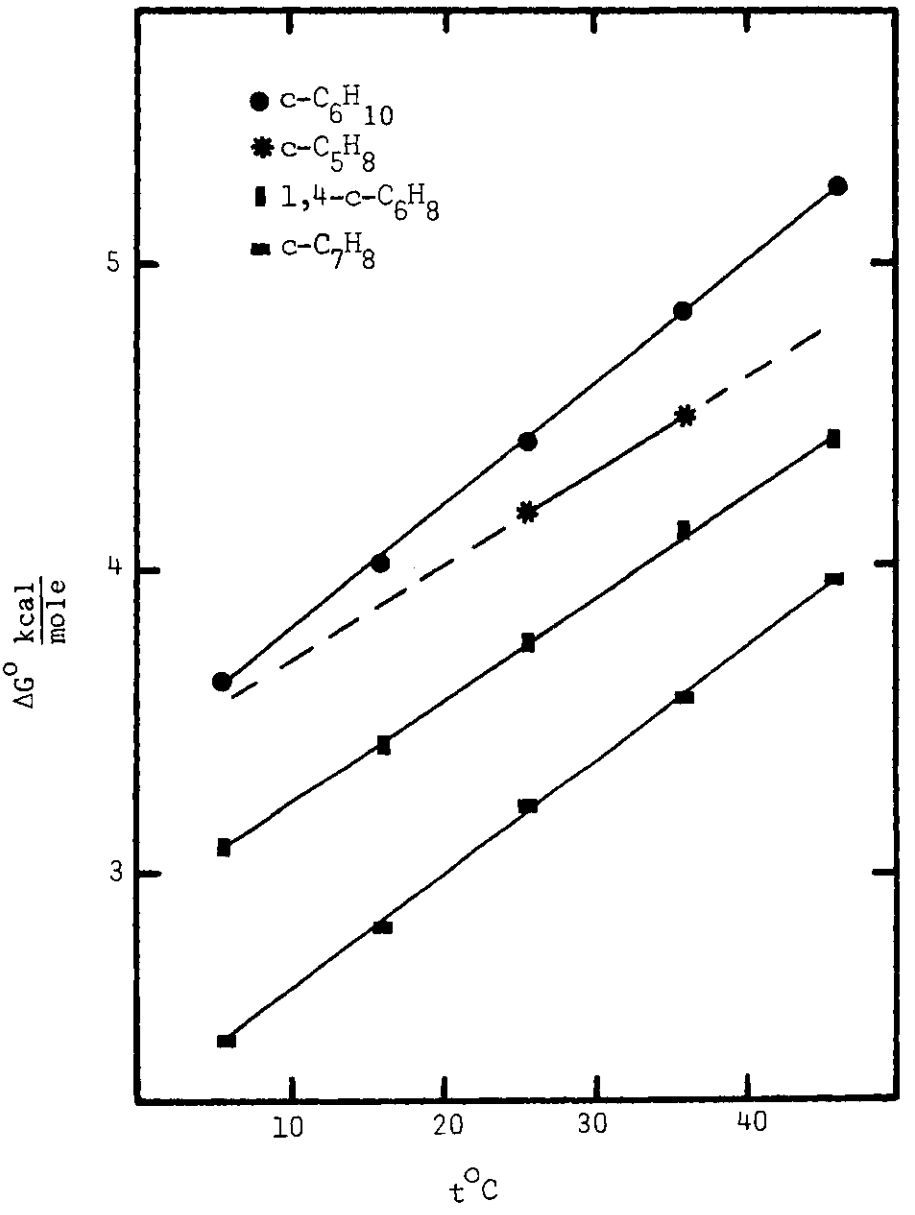


Figure 18. ΔG^{o} of Solutes in H_2O as a Function of Temperature.

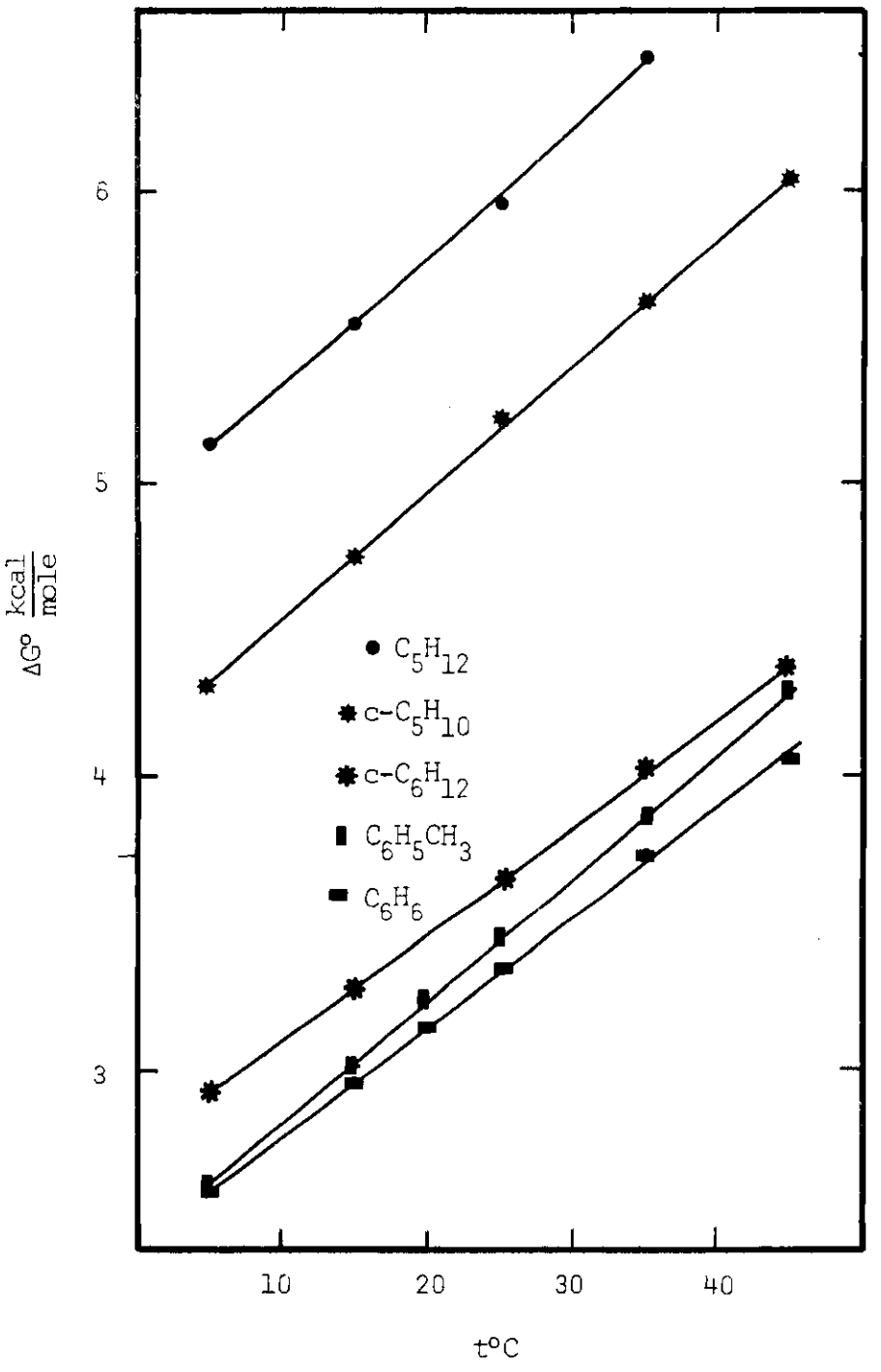


Figure 19. ΔG° of Solutes in D_2O as a Function of Temperature.

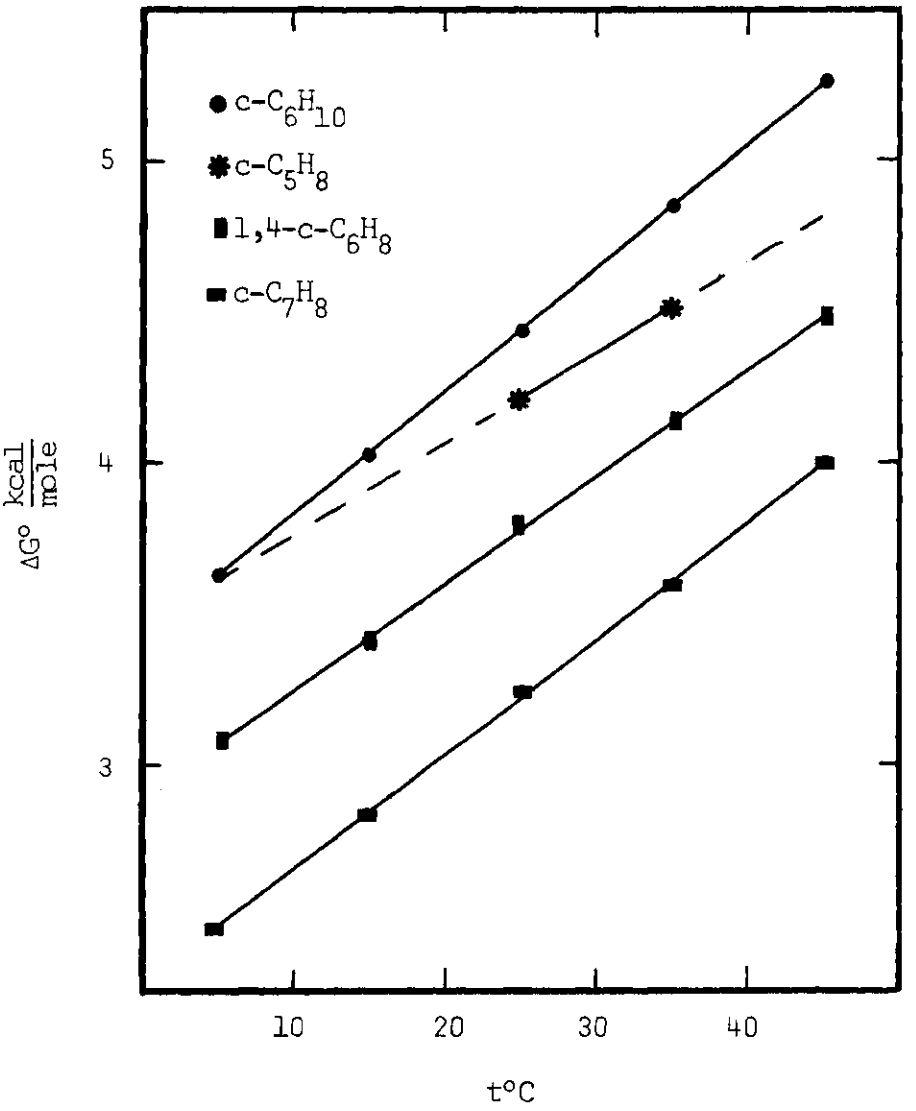


Figure 20. ΔG^{O} of Solutes in D_2O as a function of Temperature.

Some general comments can be made concerning the results reported here, in that the Henry's Law constant increases with increasing size (see Tables 6., 7., 19., and 20.) within the three families studied; aromatics, cycloalkenes, and cycloalkanes. And for molecules of about the same size, the Henry's Law constant decreases as the degree of unsaturation increases. Thus, benzene is more soluble than cyclohexene, which is more soluble than cyclohexane (all considered at unit pressure of the solute). The results for the variation of ΔG_T^o with temperature for the various solutes in H_2O and D_2O are shown in Figures 17., 18., 19., and 20.

Standard Enthalpies of Solution

The variation of ΔH_T^o with temperature for the various solutes in H_2O and D_2O are shown in Figures 21., 22., 23., and 24. The curves represent the values of the enthalpy derived from the experimental data by carrying out the proper mathematical operations. The manner in which these operations are carried out determines in part, the values derived for ΔH_T^o from the experimental data.

Since the enthalpy involves the first derivative of the logrithm of the Henry's Law constant, with respect to reciprocal temperature, and since this is almost linear, the value of ΔH^o in the middle of the temperature range ought to be reliable, regardless of the functional representation used as long as it fits the data reasonably well. The values reported here at 25^oC are felt to be as reliable as the precision which is $\pm$ 100 cal./mole.

The heats of solution in general, follow the trend that within the three families studied,the heat increases with increasing size of

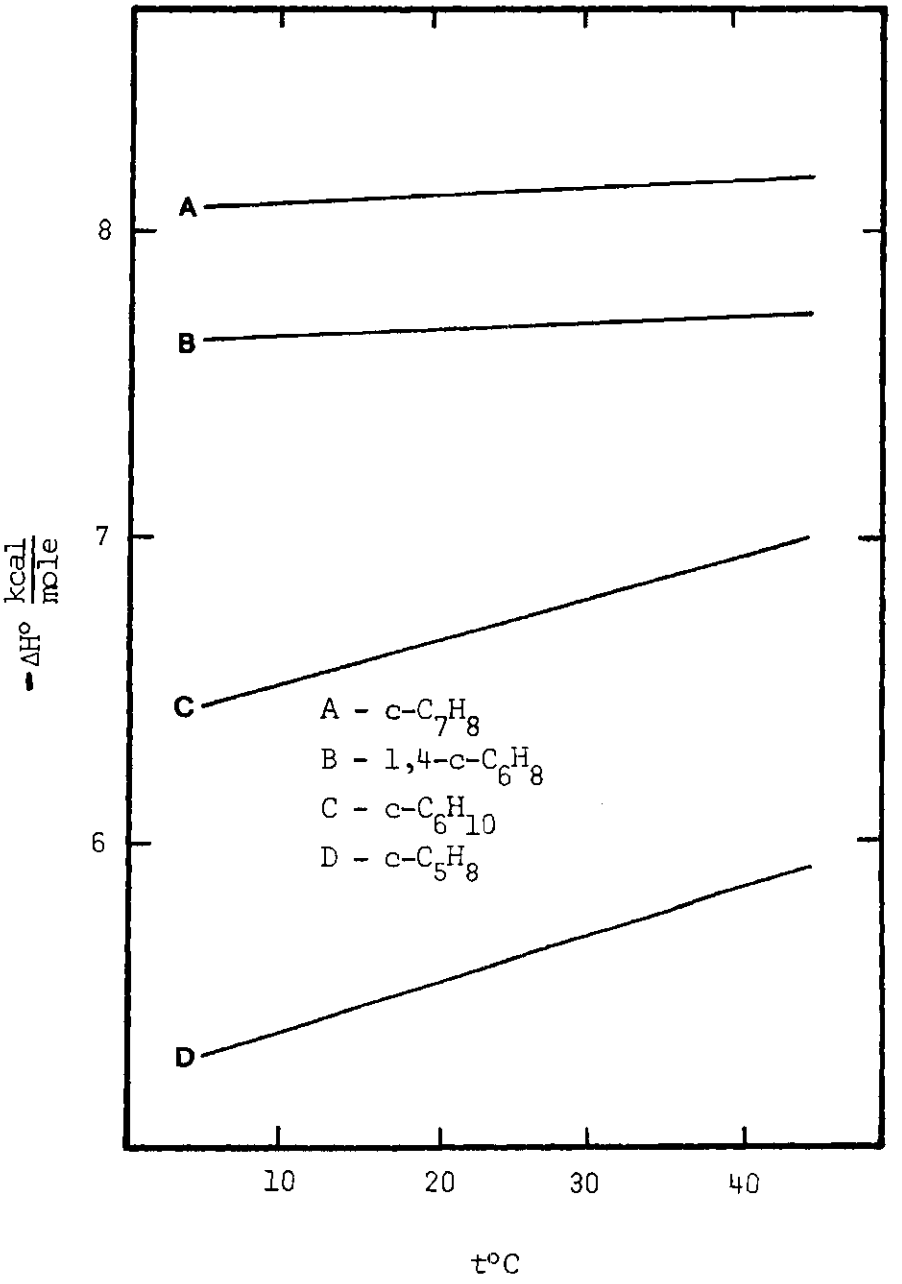


Figure 21. ΔH^{o} of Solutes in H_2O as a Function of Temperature.

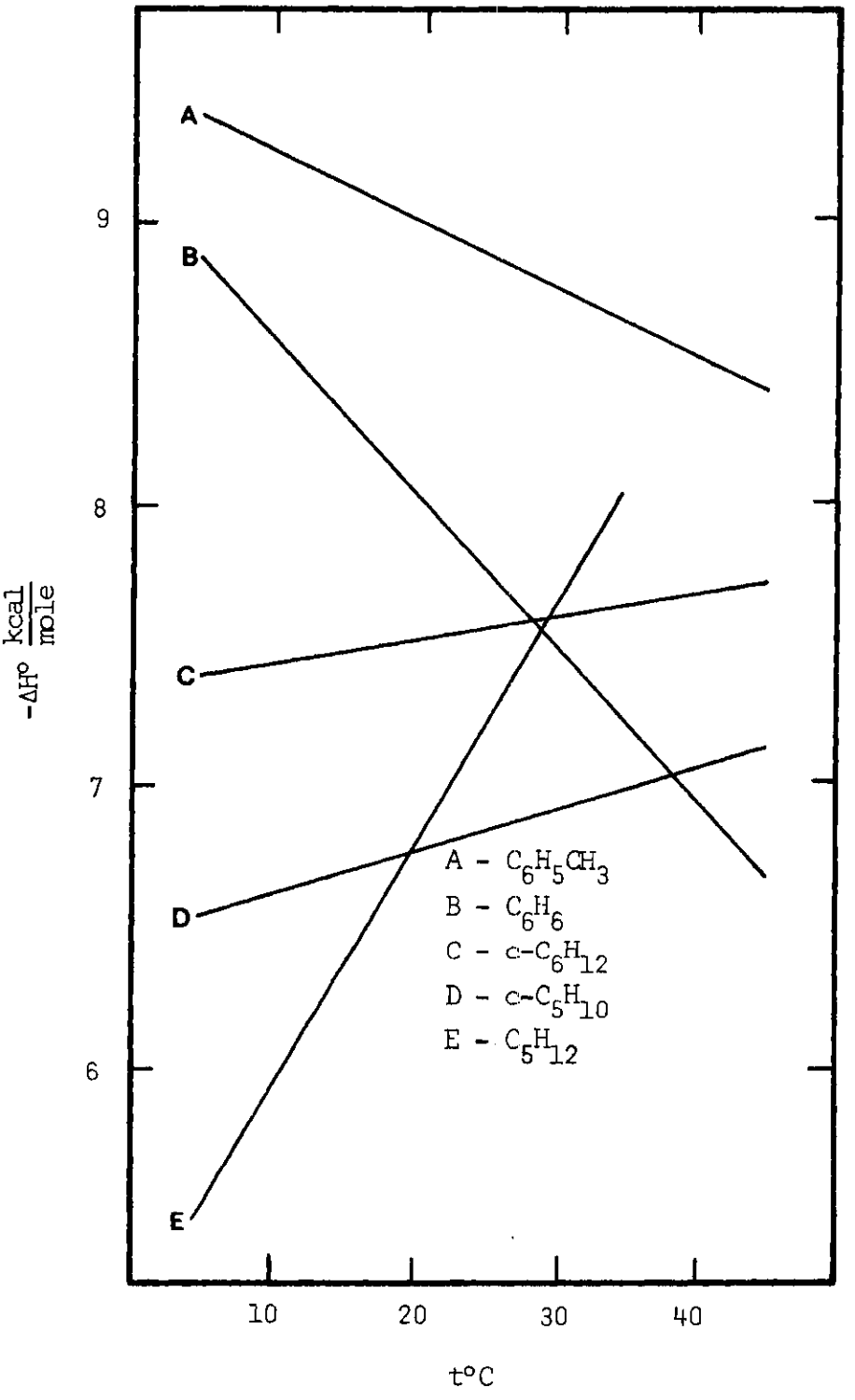


Figure 22. ΔH^O of Solute in H_2O as a Function of Temperature.

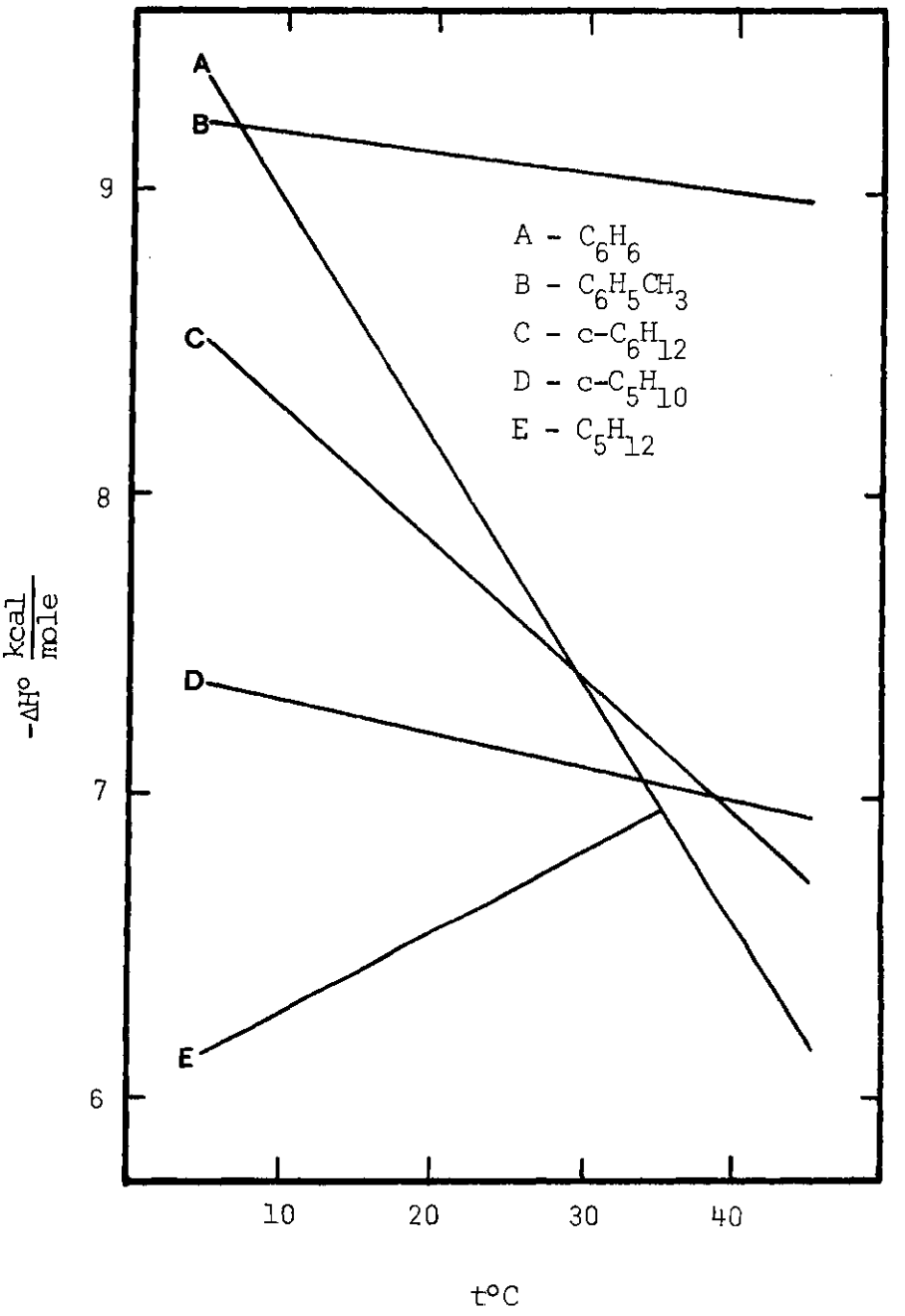


Figure 23. $\Delta H°$ of Solutes in D_2O as a Function of Temperature.

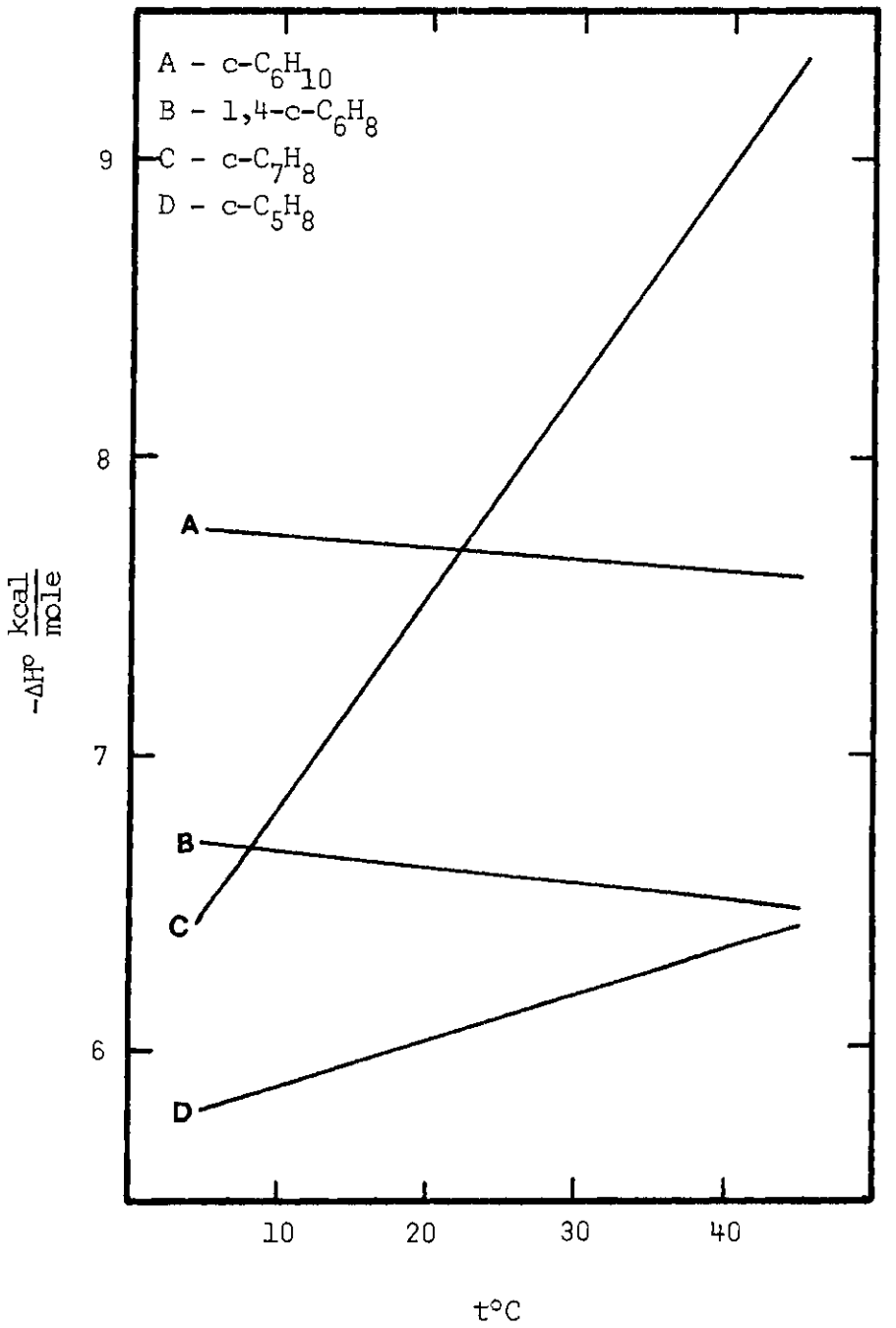


Figure 24. ΔH° of Solutes in D_2O as a Function of Temperature.

the solute. For molecules of approximately the same size, the heat tends to increase with increasing degree of unsaturation; although this is not as marked an effect as the change in heat with respect to increasing size (increasing number of CH or CH_2 groups).

Standard Heat Capacities of Solution

The heat capacity is derived from the experimental data by determining the second derivative of the logrithm of the Henry's Law constant with respect to temperature. The graphical method of data treatment makes it exceedingly difficult to determine ΔC_p^0 unless the data are of unusual precision. The analytical method of data treatment makes it possible to routinely compute ΔC_p^o; although it may well result in values whose only significance is purely statistical. Since the uncertainties in ΔH^o are usually large, it is difficult to place much confidence in derived values of ΔC_p^o.

One comment, with respect to the values of ΔC_p^o is in order. The data of Bohon and Claussen[170] for the toluene-water system, is almost identical to the result reported here, with the exception of the highest temperature point. Their data were originally treated by Herington[129] who found that the ln K data were linear, with respect to 1/T and hence, ΔC_p^o was either zero or at least, the data were unable to yield it. Glew and Robertson[165], and Wauchope and Haque[174], have reanalyzed the data of Bohon and Claussen[170], and report $\Delta C_{P,25^oC}^o$ of 84 $\pm$ 2 cal./mole-deg., the value reported here is about 25^ocal./mole. A value of the order of 80 cal./mole-deg., seems more reasonable for theoretical reasons, but it is a matter of concern as to whether the experiment or the fitting technique is yielding the

result. It is very probable that the theoretical values generated by a theory such as the scaled particle theory are better than any number yet obtained experimentally from the temperature dependence of hydrocarbon solubility in water.

Transfer Properties $(H_2O) \rightarrow (D_2O)$

The ratio of the solubilities of substances in H_2O to D_2O yields the values of the transfer properties. For this reason, many of the possible systematic errors, which may occur in the measurements of the solubilities in H_2O and D_2O should be cancelled out. Table 25. shows the molar, mole fraction, and Henry's Law constant ratio of the solubilities in D_2O to that in H_2O of all the presently available data.[65,66,163,240] From the data given in Table 24. it is apparent that the unsaturated hydrocarbons are more soluble in D_2O than H_2O. There seems to be a trend indicating a decreased solubility in H_2O as the degree of unsaturation increases (see C_6 compounds). For straight chain hydrocarbons, it appears that the solubility in H_2O decreases as the chain length increases. The results presented in this work, reference 200, are consistent with the findings of Kresheck, Schneider, and Scheraga[163] and Ben-Naim, Wilf and Yaacobi.[166] The data of Guseva and Parnov[240] were determined at higher temperatures, and have been extrapolated to 25°C in this work, and included for completeness.

The heats of transfer determined in this work are generally small, and in all cases are less than a kilocalorie. Although most of the heats are negative, no clear cut trend is apparent. In fact, the temperature dependence of ΔH^o is such that for all substances

Table 24. Comparisons of the Temperature where $\Delta H^{O}_{T,X_2} = 0$ for Benzene in H_2O.

T_K^O	Reference
283.5*	118
288.4	164
288.7	200
289.1	170
289.6	171
315.5*	166

Average Value	292.5
Standard Deivation	± 11.5
*Average Value	289.0
Standard Deivation	± 0.5

*These values were discarded, reference 166 the temperature dependence is not consistent with all others and reference 118 did not experimentally cover this temperature.

Table 25. The Ratios of the Solubility of Various Solutes in D_2O to That in H_2O at 25°C.

Solutes	R_K^T	R_k	R_x	R_m	Reference
Ar	.977	.926	1.08	0.971	65,66
$CH_3F^{29.4}$	-	.980	1.02	0.921	256
$CH_3Cl^{29.4}$	-	1.04	0.960	0.867	256
$CH_3Br^{29.4}$	-	1.08	0.930	0.840	256
$CH_3I^{29.4}$	-	1.10	0.910	0.822	256
$t\text{-}C_4H_9Cl^{29.4}$	-	.980	1.02	0.921	256
CH_4	.975	.943	1.06	0.955	166
C_2H_6	.980	.935	1.07	0.959	166
C_3H_8	.982	.971	1.03	0.922	163
C_4H_{10}	.982	.962	1.04	0.929	163
C_4H_{10}	-	1.00	0.998	0.898	166
C_5H_{12}	.983	.962	1.04	0.934	200
C_7H_{16}*	-	1.17	0.857	0.771	240
$C_7H_{16}^{100°}$	-	1.11	0.901	0.810	240
$C\text{-}C_5H_{10}$	1.01	1.02	0.985	0.886	200
$C\text{-}C_5H_8$	.997	1.03	0.973	0.876	200
$C\text{-}C_6H_{12}$*	-	1.14	0.881	0.792	240
$C\text{-}C_6H_{12}^{80°}$	-	1.10	0.909	0.818	240
$C\text{-}C_6H_{12}$	.995	1.01	0.988	0.889	200
$C\text{-}C_6H_{10}$	.954	1.01	0.988	0.889	200
$1,4\text{-}C\text{-}C_6H_8$	1.01	1.04	0.962	0.865	200
C_6H_6	1.02	1.11	0.904	0.813	200

Table 25 (Cont'd). The Ratios of the Solubility of Various Solutes in D_2O to that in H_2O at 25°C.

Solute	R_k^T	R_k	R_x	R_m	Reference
C_6H_6	1.02	1.10	0.913	0.821	166
$C\text{-}C_7H_8$	1.02	1.05	0.949	0.854	200
$C_6H_6CH_3$	1.02	1.11	0.902	0.812	200
$C_6H_5CH_3$*	-	1.19	0.842	0.764	240
$C_6H_5CH_3^{90^\circ}$	-	1.12	0.893	0.803	240
H_2S	1.02	1.03	0.971	0.873	271

*The values at 25°C were extrapolated from high temperature determinations.

$$R_x = \frac{X_{D_2O}}{X_{H_2O}}, \quad R_m = \frac{M_{D_2O}}{M_{H_2O}}, \quad R_k = \frac{K_{D_2O}}{K_{H_2O}} = R_x^{-1}$$

studied, the heat goes through zero and hence, a change of sign at some temperature in the range 5^{o} to 45^{o}C.

The transfer properties determined in this work are listed in Table 11. for 25^{o}C.

Partial Molar Volume Determinations

The results of the partial molar determinations are given as the partial molar volume at infinite dilution in Table 12. and the concentration dependent data are given in Appendix E. The results indicate that an OH group does not contribute significantly to the volume. Further, if one considers the calculation of the volume of the OH and NH groups by Bondi's[270] method, these groups should make the same size contribution to the volume as the CH_2 group. This seems to be in opposition to the experimental findings. Table 26. contains the partial molar volumes of various solutes in H_2O. Consulting this table indicates that the increase in volume of substances containing groups capable of H-bonding or processing high electron density is quite small compared to the increase in volume, due to a CH_2 group; indicating a strong interaction with water. The origin of this effect is not understood; however, these groups might well become part of the hydrogen bond network of water.

It is evident at this juncture, that data are needed to elucidate these effects; especially needed are the permanent gas data.

Table 26. Partial Molar Volume of Various Solutes Dissolved in H_2O at 25°C.*

Solute	$\bar{V}_2^{Theo.}$		$\bar{V}_2^{Exp.}$			
He	17.3	29.7[a]	15.5[e]			
Ar	26.2	32[a]	27.0[g]	31.7[f]		
H_2	19.6	22.7[g]	26[h]	25.2[b]		18.9[e]
N_2	32.3	33[a]	32.5[e]	40[h]		
O_2	27.3	32[a]	25.8[e]	30.4[f]	31[h]	26.6[g]
CO	33.3	36[h]	28.5[e]			
CO_2	37.8	35[a]	36.6[b]	33[h]		
CH_4	31.7	36.3[d,23°]	34.9[g]	37.4[f]	37[h]	37[s]
CH_3F	-	35.9[i]				
CH_3Cl	-	46.2[i]				
CH_3Br	-	53.0[i]				
CH_3I	-	63.7[i]				
HCOOH	-	33.49[o]	34.1[q]	34.7[w]		
$HCONH_2$	-	38[w]				
CH_3OH	23.4	38.13[c,20°]	38.05[j,20°]	38.68[t]		
CH_3NH_2	-	40[r]	41.6[q]	41.6[w]		
NH_2CONH_2	-	44.17[p]				
CH_2Cl_2	-	64.61[c]				
C_2H_6	43.2	50.5[d,23°]	51.8[g]	53.3[f]		
CH_3COOH	-	50.45[o]	52.0[q]	50.7[w]		
C_2H_5OH	34.9	55.08[c,20°]	54.97[j,20°]			

Table 26 (Cont'd). Partial Molar Volumes of Various Solutes Dissolved in H_2O at 25°C.*

Solute	$\bar{V}_2^{Theo.}$	$\bar{V}_2^{exp.}$		
CH_3CONH_2	-	55[w]		
CH_3NCH_3	-	58.8	59.1[q]	
CH_2OHCH_2OH	-	55.76[l,20°]		
C_2H_5COOH	-	67.9[q,w]		
C_3H_7OH	48.1	70.52[c,20°]	70.20[j,20°]	
$i\text{-}C_3H_7OH$	-	71.73[j,20°]		
$C_3H_7NH_2$	-	71.3[w]		
$C_2H_5CONH_2$	-	71.0[w]		
$CH_2OHCHOHCH_3$	-	73.71[l]		
$CH_2OHCH_2CH_2OH$	-	72.55[l]	71.44[c,20°]	
C_3H_7COOH	-	83.82[o]	84.79	84.3[w]
$i\text{-}C_3H_7COOH$	-	84.5[w]		
C_4H_9OH	62.2	86.3[c,20°]	85.77[j,20°]	85.9[k]
$i\text{-}C_4H_9OH$	-	86.42[j,20°]	86.15[k]	
$s\text{-}C_4H_9OH$	-	86.63[j,20°]	86.33[k]	
$t\text{-}C_4H_9OH$	-	87.95[k]		
$C_4H_9NH_2$	-	88.4[w]		
$C_3H_7CONH_2$	-	87.[w]		
$CH_2OHCH_2CHOHCH_3$	-	90.33[l,30°]		
$CH_2OHCH_2CH_2CH_2OH$	-	88.98[l]		
C_4H_9COOH	-	99.5[w]		
$i\text{-}C_4H_9COOH$	-	100.6[w]		
$C_5H_{11}OH$	76.2	101.80[c, 20°]	101.92[j, 20°]	

Table 26 (Cont'd). Partial Molar Volume of Various Solutes Dissolved in H_2O at 25°C.*

Solute	$\bar{V}_2^{Theo.}$	$\bar{V}_2^{exp.}$		
benzene	83.05	83.6[n]	83.2[d]	
phenol	-	86.0[q]	80.13[z]	84[w]
1,2-dihydroxy-benzene	-	87.08[n]		
1,3-dihydroxy-benzene	-	88.67[n]		
1,4-dihydroxy-benzene	-	88.90[n]	87.0[w]	
1,2,3-trihydroxy-benzene	-	88.53[n]		
1,3,5-trihydroxy-benzene	-	91.77[n]	89.1[w]	
4-amino-phenol	-	94.95[n]		
4-amino-aniline	-	92.17[n]		
nitrobenzene	-	97.71[m]		
4-fluorophenol	-	87.7[y]		
3-nitrophenol	-	99.71[x]		
4-nitrophenol	-	98.23[x]		
toluene	99.18	100.34[n]	97.71[m]	
benzylalcohol	-	100.82[j,20°]		
2-methylphenol	-	102.10[n]		
3-methylphenol	-	103.15[y]		
4-methylphenol	-	103.14[y]		
benzoic acid	-	98.77[m]		
benzaldehyde	-	96.08[m]		

Table 26 (Cont'd). Partial Molar Volumes of Various Solutes Dissolved in H_2O at 25°C.*

Solute	$\bar{V}_2^{Theo.}$	$\bar{V}_2^{Exp.}$	
3-formylphenol	-	97.87[x]	
4-formylphenol	-	96.94[x]	
2-aminobenzoic acid	-	96.7[w]	
3-aminobenzoic acid	-	90.3[w]	
4-amionbenzic acid	-	97.3[w]	
3-hydroxyansole	-	106.83[y]	
4-hydroxyansole	-	107.21[y]	
p-xylene	114.85	115.80[n]	
2,5-xylenol	-	119.06[n]	
3,4-xylenol	-	118.52[n]	
4-methylbenzyl-alcohol	-	118.13[n]	
phenylalanine	-	121.3[w]	
cumene	-	130.00[n]	
4-t-butylphenol	-	145.45[n]	
benzenethiol	-	94.09[z]	
THF	-	76.9[o]	76.9[v]
2-methyl THF	-	94.00[v]	
THFA	-	92.4[u]	93.8[v]
2,5-dimethylTHF	-	111.00[v]	
THP	-	90.6[u]	91.8[v]
THPA	-	106.8[u]	108.1[v]
1,4-dioxane	-	78.9[u]	81.[v]
1,3-dioxolane	-	65.32[v]	

Table 26 (Cont'd). Partial Molar Volumes of Various Solutes Dissolved in H_2O at 25°C.*

Solute	$\bar{V}_2^{Theo.}$	$\bar{V}_2^{Exp.}$
aziridine	- 48.87[V]	
pyridine	- 76.7[W]	
pyrrolidine	- 77.77[V]	
1-methylpyrrolidine	- 97.29[V]	
azetidine	- 63.71[V]	
piperidine	- 92.53[V]	94.9[W]
1-methylpiperidine	- 110.54[V]	
hexamethyleneimine	- 105.55[V]	
hepamethyleneimine	- 120.09[V]	
piperazine	- 80.7[W]	

(a) 154
(b) 155
(c) 186
(d) 187
(e) 188
(f) 189
(g) 190
(h) 195
(i) 242
(j) 243
(k) 244
(l) 245
(m) 246
(n) 200
(o) 247
(p) 248
(q) 249
(r) 250
(s) 8
(t) 251
(u) 252
(v) 253
(w) 254
(x) 126
(y) 268
(z) 269

*$\bar{V}_2^{Theo.} = \bar{V}_c$ for aromatics and the units of volume are cc/mole.

Theoretical Analysis and Calculations

The results of the analysis indicate that the diameters of molecules acting either as solutes or solvents, vary smoothly with polarizability as indicated by Figure 14. which contains the results for the n-alkanes, the n-alkylalcohols and n-alkylamines. In the case of the n-alkylhalides, each series is given by a smooth curve which lies below that for the n-alkanes in the decreasing order F,Cl,Br, and I. Furthermore, it appears that the perfluoro-n-alkanes are given by a curve which lies above the n-alkane curve, but it is a member of a family of similar curves. These results indicate that by determining the solubility of the rare gases in several members of a series of compounds, we can define the curve, σ versus polarizability, and thus extract the diameters of the remaining members of the series of compounds.

Once the molecular diameters have been determined, the interaction parameters can be determined as indicated in Chapter IV and plotted $(\varepsilon_2/k)^{1/2}$ versus α, and the interaction parameters for the remaining members of the series can be extracted.

The results of the theoretical calculations are shown in Appendices G and H, and in general, the results are in good agreement with the experimental results. In particular, the sizes and interaction parameters for the n-alkanols obtained in this work predict the observed Gibbs free energy and heat of solution in water and the observed partial molar volumes of the solutes in non-polar solvents.

In a recent paper de Ligny and van der Veen[67], have examined Pierotti's Theory for the solubility of gases in liquids. They found that the theory described the solubilities satisfactory, but described

the entropies less well. The improvements made in the theory in this work have, in fact allowed the correct prediction of the change in entropy with size. However, it appears that the enthalpy and entropy of interaction have been improperly separated, in view of the results for the non-polar solvents. The results for water are apparently unaffected, due to the smaller size of the thermal expansion coefficient. This situation should be easily corrected by expanding the density about the melting point where $\bar{S}_i$ is assumed to be zero, and it is recommended that this be done in some future work. Further, de Ligny and van der Veen[67], noted that the enhanced solubilities of some solutes in solvents are due to electron-donor-acceptor interactions. And they have attempted to evaluate the electron-donor-acceptor association constants.

As stated earlier, in general the theory works well; however, it does not predict the properties for cyclic and unsaturated systems in water. In extracting sizes and interaction parameters for the compounds studied in this work using equation 4-25 and selecting an interaction parameter to generate the observed thermodynamic properties; the sizes are small and the interaction parameters are reasonable. These parameters do not predict the partial molar volumes. If larger sizes are used then the free energies and heats of solution predicted are in poor agreement, indicating that in these solutions there is some type of complex formed. The notion that aromatics associate in some form of H-bonding complex has been recognized by Pimentel and McClellan,[26] Christian et.,[255] Karlsson,[24] Franks et al.,[118] Bohon and Claussen,[170] and Guseva and Parnov.[204]

In calculating the thermodynamic solution properties of H_2O and D_2O in various solvents, again the theory fails to predict the observed thermodynamic properties for the cyclic and unsaturated substances. The calculated thermodynamic solution properties for H_2O are given in Table 27., and the experimental values in Appendix K. And for D_2O the calculated properties are given in Table 28., and the experimental values in Appendix L. The theory does not take account of any specific complex-type interactions; thus it is not surprising that the theory fails to account for the thermodynamic solution properties of these compounds. It is interesting to note that if the solvent size (determined from the solubility of rare gases) for benzene, toluene, or m-xylene is used, the value calculated for $\tilde{V}_C$ for these substances in H_2O is approximately equal to the observed partial molar volume at infinite dilution.

An interesting result of equation 4-25 is shown in Figure 25., where $(1+\alpha pT)\Delta G_s - \Delta H_s$ is plotted versus the solute size σ_2 for H_2O. This figure allows one to estimate either the free energy, the heat, or solute size, if any two of the three values are known.

The calculated values of the transfer properties from H_2O to D_2O are in reasonably good agreement with the observed values of the ratio of the Henry's Law constants and are given in Table 25. In this case, the specific interactions for the aromatics and unsaturated compounds are probably nearly equal in both solvents and cancel out.

In a series of papers Battino, Wilhelm et al.,[258-259] have determined the Lennard-Jones parameters for various solvents and calculated the solution properties for some of these systems.

Table 27. Calculated Thermodynamic Properties of H_2O Dissolved in Various Solvents at 25°C.

Solvent	ΔG	-ΔH	-ΔS	$\bar{V}_2$
C_5H_{12}	2581	1991	15.3	30.2
C_6H_{14}	2547	2025	15.3	28.5
C_7H_{16}	2429	2168	15.4	26.6
C_8H_{18}	2365	2223	15.4	27.2
C_9H_{20}	2311	2266	15.4	27.3
$C_{10}H_{22}$	2271	2231	15.1	27.3
$C_{12}H_{26}$	2164	2300	14.0	28.8
$C_{14}H_{30}$	2132	2163	14.4	29.5
$C\text{-}C_6H_{12}$	2527	2400	16.5	27.8
C_6H_6	2814	2038	16.3	24.7
$C_6H_5CH_3$	2597	2480	17.0	24.6
$m\text{-}C_6H_4(CH_3)_2$	2477	2588	17.0	24.5
C_6H_5Cl	2009	3429	18.2	21.7
CCl_4	2623	2370	16.8	24.0

*The units ΔG (cal/mole), ΔH (cal/mole), ΔS (cal/mole deg) and $\bar{V}_2$ (cc/mole).

Table 28. Calculated Thermodynamic Properties of D_2O Dissolved in Various Solvents at 25°C.*

Solvent	ΔG	-ΔH	-ΔS	$\bar{V}_2$
C_6H_{14}	2393	2243	15.6	27.5
C_7H_{16}	2394	2216	15.5	28.1
$C\text{-}C_6H_{12}$	2488	2453	16.6	27.6
C_6H_6	2776	2091	16.3	24.5
$C_6H_5CH_3$	2558	2523	17.1	24.4
$m\text{-}C_6H_{14}(CH_3)_2$	2436	2640	17.0	24.2
CCl_4	2585	2422	16.8	23.8
C_6H_5Cl	1968	3484	18.3	21.6

*The units are ΔG (cal/mole), ΔH (cal/mole), ΔS (cal/mole deg) and $\bar{V}_2$ (cc/mole).

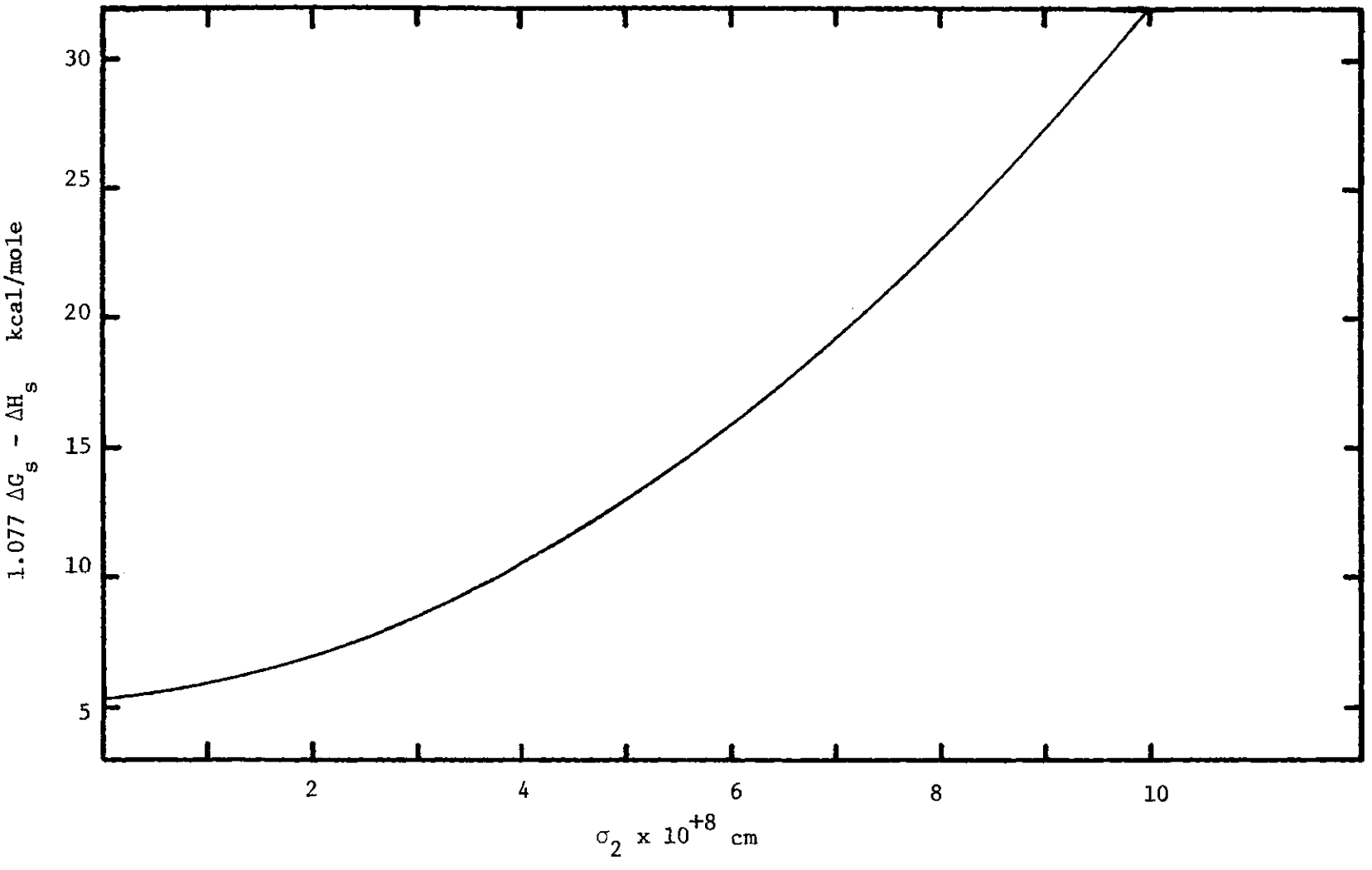


Figure 25. Plot of $(1 + \alpha_p T)\Delta G_s - \Delta H_s$ versus σ_2 for the Solvent H_2O.

However, they have made no effort to improve the theory or to evaluate solute Lennard-Jones parameters. Their findings are in general agreement with the results presented here for the Lennard-Jones parameters for solvents.

CHAPTER VI

RECOMMENDATIONS AND CONCLUSIONS

The solubility of nine relatively small rigid organic molecules in H_2O and D_2O have been studied as a function of temperature over the range $5^{\circ}C$ to $45^{\circ}C$. A gas chromatographic technique was used in the studies and the technique has been pushed to its practical limit as a quantitative tool for such studies. The method is simple to use and is capable of measuring the solubilities of very sparingly soluble organic substances in water. The limit of detection and identification of the chromatographic technique is much less than that required for quantitative determination; and thus, the present study was limited to those substances which were sufficiently soluble to permit quantitative measurements. This limit is approximately ten parts per million by weight.

In general, it was found that the technique could not produce solubility measurements better than $\pm$ three percent. While this is adequate for an absolute solubility measurement, it appears to be marginal for studies aimed at determining temperature derivatives of the solubility. In order to adequately provide such measurements it would require an order of magnitude increase in the precision of the technique, which using present chromatographic procedures is not possible. In any event, solubilities have been determined and reliable heats of solution at $25^{\circ}C$ are reported. The temperature dependence of the heats of solution must be viewed with caution.

The partial molar volumes of sixteen relatively rigid organic molecules have been evaluated at 25°C in H_2O. The method of determination used a magnetic float densimeter. The overall accuracy of the measurements was in general better than $\pm$ one percent. This method of volume determination allows the accurate determination of the volume for slightly soluble compounds; and will allow the investigation of steric effects. This method should be employed to investigate families of aromatic compounds. This information along with volumes data for the missing permanent gases should aid in evaluating the form of the interaction necessary to account for complex formation between aromatic substances and H_2O.

The solvent and solute Lennard-Jones parameters determined in this work, in general, do a particularly good job of predicting thermodynamic solution properties. However, no attempt was made here to refine these parameters; which, in fact should be done. Further, the solubility of the rare gases should be determined in a large number of substances in order to fully develop the polarizability-size equations for series of compounds. The methods presented here, based on the thermodynamic solution properties, should facilitate the extraction of Lennard-Jones parameters for a large number of substances.

APPENDIX A

Antoine Constants

APPENDIX A
Antoine Constants*

Substance	A	B	C
butane	6.80896	935.86	238.72
pentane	6.87632	1075.78	233.205
hexane	6.87024	1168.72	224.210
heptane	6.89385	1264.37	216.636
octane	6.90940	1349.82	209.385
nonane	6.93440	1429.46	201.820
decane	6.96375	1508.75	195.374
undecane	6.97220	1569.57	187.700
dodecane	6.99795	1639.27	181.835
tridecane	7.00756	1690.67	174.220
tetradecane	7.01300	1740.88	167.20
cyclopentane	6.88676	1124.162	231.361
cyclopentene[a]	6.92066	1121.818	233.446
cyclohexane	6.84130	1201.531	222.647
cyclohexene[a]	6.88617	1229.973	224.104
1,4-cyclohexadiene[b]	-	-	-
cycloheptane[c]	6.85271	133.0742	216.246
cycloheptatriene[c]	6.97032	1374.656	220.538
benzene	6.90565	12 11033	220.790

APPENDIX A (CONT'D)

Antoine Constants*

Substance	A	B	C
toluene	6.95464	1344.800	219.482
o-xylene	6.99891	1474.679	213.686
m-xylene	7.00908	1462.266	215.105
p-xylene	6.99052	1453.430	215.307
ethylbenzene	6.95719	1424.255	213.206
n-propylbenzene	6.95142	1491.297	207.140
i-propylbenzene	6.93666	1460.793	207.777
n-butylbenzene	6.98317	1577.965	201.378
i-butylbenzene	6.92804	1525.446	204.122
s-butylbenzene	6.94866	1539.223	205.052
t-butylbenzene	6.91829	1503.651	203.281
1,2,3-trimethyl-benzene	7.04082	1593.958	207.078
1,2,4-trimethyl-benzene	7.04383	1573.267	208.564
1,3,5-trimethyl-benzene	7.07436	1569.622	209.578

*Unless otherwise noted all values were taken from API Tables Project 44. The Antoine equation is written as

$$\log_{10} P = A - B/(t+c), \text{ where } t \text{ is in } {}^{o}C.$$

a) See reference 108.
b) See Appendix V.
c) See reference 107.

APPENDIX B

Critical Constants of Solutes

APPENDIX B

Critical Constants of Solutes

Substance	P_c atm	t_c °C
pentane	33.25[a]	196.5[a]
cyclopentane	44.49[a]	238.5[a]
cyclopentene	47.28[b*]	232.9[a]
cyclohexane	40.2[a]	280.3[a]
cyclohexene	42.86[b*]	287.26[a]
cyclohexadiene[c]	-	-
benzene	48.34[a]	288.94[a]
toluene	40.55[a]	318.57[a]
cycloheptatrienedd	-	-

*Estimated

a) See Reference 115
b) See Reference 114
c) See Appendix IV
d) Experimental Virial Coefficient Used, See Note C, Appendix I

APPENDIX C

Various Thermodynamic and Physical Properties of Substances

APPENDIX C-1

Various Thermodynamic and Physical Properties of Substances*

Substance	$\bar{V}$ 25°C cc/mole	$\alpha_T \times 10^2$[a] $(deg.)^{-1}$	$\Delta H^\circ_{vap,25^\circ C}$ cal/mole
propane	89.84	0.3125	3969
butane	101.43	0.2024	5191
pentane	116.104	0.1561	6395
hexane	131.598	0.1393	7568
heptane	147.456	0.1251	8784
octane	163.530	0.1154	9916
nonane	179.670	0.1070	11,100
decane	195.905	0.1046	12,277
undecane	212.217	0.1010	13,465
dodecane	228.579	0.09474	14,648
tridecane	244.924	0.09353	15,830
tetradecane	261.312	0.09431	17,010
2,2-dimethylpropane	123.31	0.2017	5205
3-methylpheptane	162.770	0.1160	8100
2,3-dimethylhexane	161.313	0.1144	9272
2,4-dimethylhexane	164.068	0.1195	9027
2,2,4-trimethyl-pentane	166.069	0.1198	8396
cyclopentane	94.713	0.1332	6845
cyclopentene	88.860	0.1425	6835[c]

APPENDIX C-1 (CONT'D)

Various Thermodynamic and Physical Properties of Substances*

Substance	$\bar{V}$ 25°C cc/mole	$\alpha_T \times 10^2$[a] $(deg.)^{-1}$	$\Delta H^o_{vap,25^oC}$ cal/mole
cyclohexane	108.744	0.1204	7908
methylcyclohexane	128.34	0.1130	8451
cyclohexene	101.899	0.1208	8065 *C-2
1,4-cyclohexadiene	94.58[d] 20°	0.1210	8100[e]
cycloheptane	121.72	0.1091	9210[b]
cycloheptatriene	103.83[d] 19°	0.1290	9250[b]
benzene	89.399	0.1216	8102
toluene	106.846	0.1078	9083
o-xylene	121.193	0.09681	10,381
m-xylene	123.456	0.09931	10,195
p-xylene	123.919	0.1018	10,128
ethylbenzene	123.064	0.1015	10,097
n-propylbenzene	140.110	0.09886	11,049
n-butylbenzene	156.771	0.09485	11,980
i-propylbenzene	140.157	0.09982	10,789
1,2,3-trimethyl-benzene	134.974	0.08850	11,726
1,2,4-trimethyl-benzene	137.860	0.09222	11,458
1,3,5-trimethyl-benzene	139.571	0.09453	11,348
i-butylbenzene	158.069	0.09752	11,820
s-butylbenzene	156.430	0.09557	11,830

APPENDIX C-1 (CONT'D)

Various Thermodynamic and Physical Properties of Substances*

Substance	$\bar{V}$ 25°C cc/mole	$\alpha_T \times 10^2$[a] $(deg.)^{-1}$	$\Delta H^o_{vap,25°C}$ cal/mole
t-butylbenzene	155.626	.09508	11,730

APPENDIX C-2

Various Thermodynamic and Physical Properties of Substances*

Substance	$\bar{V}$ 25°C cc/mole	$\alpha_T \times 10^2$ $(deg.)^{-1}$	$\Delta H^o_{vap,25°C}$ cal/mole
bromobenzene	105.51	.0960	10,170
chlorobenzene	102.21	.0980	10,870
fluorobenzene	94.03	.1220	7,996
iodobenzene	111.91[h]	.0870[f]	10,377[d]
nitrobenzene	102.73	.0830	12,540
phenol	$87.41^{20°}$	.0850	13,820
aniline	91.53	.0831	13,325
benzenethiol	102.71	.0899	10,840
cyclohexanol	103.43	.0770	14,820
cyclohexylamine	115.26	.1164	10,926
perfluorobenzene	115.79	.1410	8,530
perfluoromethyl-cyclohexane	195.80[g]	.1590[g]	7,830[g]
perfluoro-n-pentane	225.87[h]	.1560[h]	8,240[i]

APPENDIX C-2 (CONT'D)

Various Thermodynamic and Physical Properties of Substances*

Substance	$\bar{V}$ 25°C cc/mole	$\alpha_T \times 10^2$[a] $(deg.)^{-1}$	$\Delta H^o_{vap,25°C}$ cal/mole
methanol	40.73	.120	8946
ethanol	58.69	.110	10,112
propanol	75.14	.0960	11,310
butanol	91.97	.0940	12,540
pentanol	108.63	.0920	13,610
hexanol	125.23	.0870	14,800
heptanol	141.96	.0953	16,000
octanol	158.42	.0828	17,200
2-butanol	92.35	.0910	11,870
formic acid	37.91	.1020	4,754
acetic acid	57.54	.1110	5,505
propionic acid	74.98	.1100	13,120
butyric acid	92.43	.1030	14,470
valeric acid	109.29	.1010	16,560
propylamine	83.01	.1460	7,490
butylamine	99.56	.1250	8,366
dimethylsulfoxide	71.30	.0880	12,640
acetone	74.05	.1423	7,372
carbondisulfide	60.65	.1169	6,578
1,1,2,2,-tetra-chloroethane	105.80	.0998	10,750

APPENDIX C-2 (CONT'D)

Various Thermodynamic and Physical Properties of Substances*

Substance	$\bar{V}$ 25°C cc/mole	$\alpha_T \times 10^{2a}$ $(deg.)^{-1}$	$\Delta H^{o}_{vap,25^{o}C}$ cal/mole
1,1,2-trichloro-1,2,2-tirfluoro-ethane	119.84	.1465	6,750
perfluoro-tri-n-butylamine	358.30[d]	-	-
N-methylacetamide	76.62	-	-
hydrazine	31.70	-	-
N,N-dimethylhydrazine	7 .95[d]	-	-
carbon tetrachloride	97.09	.127	7,746

*Unless otherwise noted all values were obtained for Appendix C-1 from reference 143 and for Appendix C-2 from reference 138.

(a) Calculated from $\alpha = \frac{(d_1/d_2)-1}{t_2-t_1}$ using $t_2 = 25^{o}C$, $t_1 = 20^{o}C$.

(b) See reference 107.
(c) Estimated using the Clausius-Claperyon equation.
(d) See reference 137.
(e) Approximated by comparing the heat of varporization of cyclohexane, cyclohexene, and benzene.
(f) See reference 139.
(g) See reference 140.
(h) See reference 141.
(i) See reference 142.

APPENDIX D

Estimated Vapor Pressure for 1,4-cyclohexadiene

APPENDIX D

Estimated Vapor Pressures for 1,4-cyclohexadiene

$t^{\circ}C$	Vapor Pressure m m
5.1	28.39
15.2	47.43
25.1	75.83
35.2	118.65
45.2	179.72

The vapor pressure as a function of temperature was calculated using the Clausius-Clapeyron equation together with an assumed value of $\Delta H_v^{25^{\circ}} = 8100 \frac{cal}{mole}$.

APPENDIX E

CONCENTRATION DEPENDENT MOLAL VOLUME DATA.

APPENDIX E

Concentration Dependent Apparent Molal Volume Data for Various Solutes at 25°C in H_2O.

Solute	$m(\frac{moles}{kg})$	Δi	$\Sigma_i x10^4$
1,2-dihydroxy-benzene	0.08630	0.05283	1.0
	0.08085	0.04917	1.0
	0.05262	0.03215	0.66
	0.04502	0.02737	0.10
	0.03977	0.02428	0.73
	0.02590	0.01585	0.10
	0.01785	0.01070	0.61
1,3-dihydroxy-benzene	0.09204	0.05141	0.95
	0.06160	0.03477	0.90
	0.04677	0.02639	0.16
	0.04337	0.02434	0.33
	0.03171	0.01784	0.52
	0.02106	0.01203	0.20
	0.01251	0.00713	0.37
	0.003877	0.00215	0.28
	0.003438	0.00206	0.15
1,4-dihydroxy-benzene	0.10867	0.06167	0.40
	0.06168	0.03483	0.49
	0.06030	0.03471	0.60

APPENDIX E (CONT'D)

Solute	$m(\frac{moles}{kg})$	Δi	$\Sigma_i x10^4$
1,4-dihydroxy-benzene	0.03626	0.02064	0.22
	0.009734	0.00565	0.38
	0.004404	0.00253	0.18
	0.002552	0.00153	0.20
	0.002460	0.00120	0.70
	0.002337	0.00116	0.20
	0.001968	0.00118	0.50
1,2,3-trihydroxy-benzene	0.08299	0.08183	0.99
	0.06794	0.06739	0.33
	0.05793	0.05738	0.63
	0.05595	0.05483	0.63
	0.04741	0.04674	0.11
	0.03625	0.03589	0.68
	0.01483	0.01484	0.51
	0.008059	0.00800	0.35
	0.006670	0.00658	0.57
1,3,5-trihydroxy-benzene	0.09905	0.08903	0.44
	0.06151	0.05552	0.95
	0.04636	0.4224	0.40
	0.02385	0.02152	0.35

APPENDIX E (CONT'D)

Solute	$m(\frac{moles}{kg})$	Δi	$\Sigma_i x10^4$
1,3,5-trihydroxy-benzene	0.01554	0.01409	0.37
	0.01172	0.01064	0.77
	0.004826	0.00437	0.38
2-methylphenol	0.09246	0.01541	0.10
	0.08687	0.01439	0.37
	0.05983	0.00994	0.41
	0.02922	0.00488	0.58
	0.01533	0.00252	0.53
	0.009412	0.00155	0.17
2,5-xylenol	0.01787	0.001620	0.26
	0.01376	0.001230	0.20
	0.01308	0.001170	0.34
	0.007291	0.000650	0.61
	0.005614	0.000510	0.30
	0.00511	0.00048	0.24
3,4-xylenol	0.01168	0.00117	0.22
	0.01159	0.00126	0.24
	0.008776	0.000880	0.26
	0.004748	0.000510	0.29
	0.002638	0.000280	0.17

APPENDIX E (CONT'D)

Solute	$m(\frac{moles}{kg})$	Δi	$\Sigma_i x10^4$
4-methyl-benzylalcohol	0.01754	0.00204	0.23
	0.01236	0.00144	0.89
	0.01191	0.00133	0.36
	0.007472	0.00088	0.13
	0.005080	0.00055	0.38
	0.002799	0.00033	0.22
4-t-butylphenol	0.008631	0.00017	0.57
	0.006585	0.00014	0.53
	0.005132	0.00014	0.39
	0.003204	0.00014	0.36
	0.002070	0.00009	0.40
4-amino-aniline	0.02580	0.00919	0.32
	0.01868	0.00658	0.20
	0.008583	0.00306	0.42
	0.007544	0.00261	0.57
	0.003884	0.00134	0.31
	0.003393	0.00121	0.47
4-aminophenol	0.01855	0.00855	0.36
	0.002682	0.00118	0.18

APPENDIX F

Polarizabilities and Dipole Moments for Various Substances

APPENDIX F

Polarizabilities and Dipole Moments for Various Substances

Rare Gases

Substance	$\alpha \times 10^{-4}$ [a] cc/molecule
He	.204
Ne	.393
Ar	1.63
Kr	2.46
Xe	4.00
Rn	5.86

Substance	$\alpha \times 10^{24}$ [c] cc/molecule	μ [j] D
NH_3	2.26	1.47
H_2S	3.78	0.90
HCN	2.59	2.56
C_2H_2	3.33	-
C_2H_4	4.26	-
H_2	.802 [e]	-
D_2	.775	-
N_2	1.76	-
O_2	1.57 [e]	-
CO	1.95	0.13
NO	1.70 [e]	0.148

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

Substance	$\alpha \times 10^{24}$ [c] cc/molecule	μ [j] D
CO_2	2.65	0.18
SF_6	4.44 [f]	-
CF_4	2.52 [e]	-
SO_2	3.72	1.61
N_2O	3.00	0.18
Substance	$\alpha \times 10^{24}$ [b] cc/molecule	μ [j] D
CH_4	2.60	-
C_2H_6	4.47	-
C_3H_8	6.29	-
C_4H_{10}	8.12	-
C_5H_{12}	9.95	-
C_6H_{14}	11.78	-
C_7H_{16}	13.61	-
C_8H_{18}	15.44	-
C_9H_{20}	17.26	-
$C_{10}H_{22}$	19.10	-
$C_{11}H_{24}$	20.92	-
$C_{12}H_{26}$	22.75	-
$C_{13}H_{28}$	24.57	-
$C_{14}H_{30}$	26.40	-

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

Substance	$\alpha \times 10^{24}$[b] cc/molecule	μ[j] D
benzene	10.32	-
toluene	12.33	0.34
o-xylene	14.10	0.54
m-xylene	14.26	0.37
p-xylene	14.12	0.06
ethylbenzene	14.25	0.35
cumene	16.09	0.38
t-butylbenzene		0.41
fluorobenzene	10.28[g]	1.42
chlorobenzene	12.36[g]	1.51
bromobenzene	13.46[g]	1.50
iodobenzene	17.49[g]	1.29
nitrobenzene	12.97[g]	3.85

Substance	$\alpha \times 10^{24}$[b] cc/molecule	μ[j] D
perfluorobenzene	14.13	0-.33
perfluoro-n-heptane	14.57[i]	-
perfluoro-methyl-cyclohexane	-	-
perfluoro-tri-n-butylamine	25.82[d]	1

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

Substance	$\alpha x10^{24}$[b] cc/molecule	μ[j] D
CH_3F	2.592	1.83[k]
C_2H_5F	4.43	-
C_3H_7F	5.987	-
C_4H_9F	6.318	-
$C_5H_{11}F$	9.950	-
CH_3Cl	4.567	1.92[k]
C_2H_5Cl	6.405	1.96[g]
C_3H_7Cl	8.244	1.97[g]
C_4H_9Cl	10.08	1.90[g]
$C_5H_{11}Cl$	11.94	1.94[g]
CH_3Br	5.705	1.80[k]
C_2H_5Br	7.545	1.90[g]
C_3H_7Br	9.385	1.93[g]
C_4H_9Br	11.22	-
$C_5H_{11}Br$	13.03	-
CH_3I	7.722	1.48[g]
C_2H_5I	9.604	1.78[g]
C_3H_7I	11.44	1.84[g]
C_4H_9I	13.28	-
$C_5H_{11}I$	15.12	-

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

Substance	$\alpha \times 10^{24}$ [b] cc/molecule	μ [j] D
phenol	11.10[g]	1.45
o-cresol	12.98[g]	1.45
catechol	10.95[d]	2.60
resorcinol	-	2.09
hydroquinone	-	1.40
phloroglycinol	-	-
pyrogallol	-	-
2,5-xylenol	-	1.43
3,5-xylenol	-	1.76
p-methylbenzyl-alcohol	-	1.80
p-t-butylphenol	-	1.62
phenylenediamine	-	1.58
benzylalcohol	12.93[g]	1.66

Substance	$\alpha \times 10^{24}$ [g] cc/molecule	μ [j] D
carbon tetra-chloride	10.49	-
nitromethane	6.65	3.13
N-methylacet-amide	7.84	3.55

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

Substance	$\alpha \times 10^{24}$ [g] cc/molecule	μ [j] D
CH_3OH	3.26	1.66
C_2H_5OH	5.13	1.66
C_3H_7OH	6.96	1.66
C_4H_9OH	8.78	1.66
$C_5H_{11}OH$	10.62	1.66
$C_6H_{13}OH$	12.46	1.66
$C_7H_{15}OH$	14.30	1.66
$C_8H_{17}OH$	16.14	1.66
$C_9H_{19}OH$	17.97	1.66
$C_{10}H_{21}OH$	19.81	1.66
iC_4H_9OH	8.81	1.66
$c\text{-}C_6H_{11}OH$	11.33	1.66

Substance	$\alpha \times 10^{24}$ [h] cc/molecule	μ [j] D
CH_3COOH	5.151	0.74
C_2H_5COOH	6.961	0.63
C_3H_7COOH	8.800	0.94
C_4H_9COOH	10.64	0.63

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

Substance	$\alpha \times 10^{24}$ [d] cc/molecule	$-\chi_m$ cgs	μ [j] D
cyclopentane	9.230		-
cyclopentene	8.960		-
cyclohexane	11.06		-
methylcyclohexane	14.32		-
cyclohexene	10.78		-
1,4-cyclohexadiene	10.53		-
cycloheptatriene	12.53		-

Substance	$\alpha \times 10^{24}$ [g] cc/molecule	μ [j] D
carbon disulfide	8.57	0.06
acetone	8.67	2.83
1,1,2,2-tetrachloroethane	12.14	1.71
1,1,2-trichloro-1,2,2-trifluoro	10.37	.77
ethane	-	-
hydrazine	3.51[d]	1.90
methylhydrazine	-	1.69
N,N-dimethylhydrazine	7.42	-
dimethylsulfoxide	7.99	3.90

APPENDIX F (CONT'D)

Polarizabilities and Dipole Moments for Various Substances

a. See reference 144.
b. See reference 145.
c. See reference 55.
d. Calculated using the Lorentz-Lorentz equation; $\alpha = \left(\frac{n^2-1}{n^2+2}\right) \frac{M}{P} \left(\frac{3}{4\pi}\right) \frac{1}{N}$ where values of n are taken from reference 137.
e. See reference 52.
f. See reference 130.
g. See reference 138.
h. See reference 139.
i. See reference 140.
j. See reference 146.

APPENDIX G*

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in Polar Solvents at 25°C.

G-1 H_2O

G-2 D_2O

G-3 CH_3OH

*All Thermal Units are Calories and Volumes are cc/mole.

APPENDIX G-1

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in H_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\bar{V}_2$	ΔC_p	Ref.
He	T	6934	499	24.9	17.3	21.8	
	E	7048	428	25.1	15.5[b]	40.6	147
Ne	T	6636	1078	25.9	18.5	21.9	
	E	6934	1065	26.8		21.2	147
Ar	T	6281	2572	29.7	26.2	26.0	
	E	6274	2680	30.0	27.0[a]	32.8	149
Kr	T	6042	3349	31.5	30.1	27.6	
	E	5954	3432	31.5		34.7	147
Xe	T	5670	4366	33.7	35.0	29.3	
	E	5611	4350	33.4		32.1	147
Rn	T	5127	5864	36.9	42.8	31.8	
	E	5182	5050	36.8[f]			150
H_2	T	6712	1130	26.3	19.6	22.9	
	E	6614	985	25.5	18.9[b]	27.9	148
N_2	T	6943	2440	31.5	32.3	31.5	
	E	6720	2681	31.5	32.5[b]	38.5	148

APPENDIX G-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in H_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\bar{V}_2$	ΔC_p	Ref.
O_2	T	6421	2519	30.0	27.3	27.0	
	E	6330	2953	31.1	26.6[a]	48.0	148
NO	T	6274	2580	29.7	26.2	26.0	
	E	6091	2680	30.2[f]			150
CO_2	T	5994	4261	34.4	37.8	31.8	
	E	4387	4665	30.4	36.6[f]	33.4	148
SF_6	T	6458	7354	46.3	78.1	50.3	
CF_4	T	7436	4213	39.1	55.7	45.1	
	E	7426	2938	34.8		46.7	147
CCl_4	T	4357	9357	46.0	71.1	42.4	
	E	4376	9000[g]	41.8[f]			150
CH_4	T	6292	3204	31.9	31.7	29.2	
	E	6298	3279	32.1	34.9[a]	69.2	148
C_2H_6	T	6119	4654	36.1	43.2	34.9	
	E	6105	4650	36.1	51.2[e]	82.7	151

APPENDIX G-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in H_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\overline{V}_2$	ΔC_p	Ref.
C_3H_8	T	6230	5766	40.2	31.7	41.7	
	E	6258	5743	40.3		56.7	152
C_4H_{10}	T	6371	6822	44.3	43.2	48.5	
	E	6386	6169	42.2		123.7	151
C_5H_{12}	T	6393	7892	47.9	56.3	54.2	
	E	5964	7149	44.0			200
C_6H_{14}	T	6477	8742	51.1	70.4	59.4	
	E	6510	6853	44.8			153
C_7H_{16}	T	6545	9687	54.4	83.8	65.0	
	E	7070	8082	50.8			153
C_8H_{18}	T	6639	10549	57.7	124.1	70.4	
	E	6660	9386	53.8			153
C_9H_{20}	T	6680	11507	61.0	139.1	75.8	
$C_{10}H_{22}$	T	6684	12434	64.1	153.4	80.7	

APPENDIX G-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in H_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\bar{V}_2$	ΔC_p	Ref.
CH_3OH	T	-841.8	11421	35.5	23.4	1.45	150
	E	-805	11240	35.0	38.7[c]		
C_2H_5OH	T	-743.3	12473	39.3	34.9	10.1	150
	E	-715	12880	40.8	55.1[c]		
C_3H_7OH	T	-563.3	13473	43.3	48.1	16.9	150
	E	-556	14420	46.5	70.7[c]		
C_4H_9OH	T	-450.0	14533	47.2	62.2	23.5	150
	E	-436	15940	47.2	86.6[c]		
$C_5H_{11}OH$	T	-213.7	15364	50.8	76.2	30.1	150
	E	-207	17500	58.0	102.2[c]		
$C_6H_{13}OH$	T	- 97.76	16260	54.2	90.0	35.8	
	E	- 93.54					150
$C_7H_{15}OH$	T	-180.6	17388	57.7	104.3	41.0	
$C_9H_{19}OH$	T	-474.2	19800	64.2	131.8	49.7	

APPENDIX G-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in H_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\bar{V}_2$	ΔC_p	Ref.
$C_{10}H_{21}OH$	T	-747.4	20801	67.3	145.5	53.5	
$C_2H_5NH_2$	T	-488.3	12668	40.9	40.3	13.5	
	E	-328	12910	42.2			150
C_6H_6	T	3281	7733	36.9	38.2		
	E	3292	7722	36.9	83		200
$C_6H_5CH_3$	T	3353	8890	41.1	51.3		
	E	3369	8860	41.0			200
$C_6H_5C_2H_5$	T	3496	9751	44.4	63.1		
	E	3478	9770	44.4			170
$mC_6H_4(CH_3)_2$	T	3445	9753	44.3	62.4		
	E	3439	9754	44.3			170
$pC_6H_4(CH_2)_2$	T	3450	9746	44.3	62.4		
	E	3462	9727	44.2			170
$iC_6H_5C_3H_7$	T	3730	10060	46.3	70.3		
	E	3682	9983	45.84			165

APPENDIX G-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in H_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\overline{V}_2$	ΔC_p	Ref.
	T	5188	7521	42.6	6.15		
C-C_6H_{12}	E	5189	7511	42.6			200
	T	4410	7649	40.5	52.1		
C-C_6H_{10}	E	4429	7632	40.5			200
	T	3660	7467	37.3	40.3		
1,4-c-C_6H_8	E	3644	7493	37.4			200
	T	3233	8216	38.4	42.5		
C-C_7H_8	E	3223	8227	38.4			200
	T	3640	6706	34.7	32.7		
C-C_5H_{10}	E	3625	6715	34.7			200
	T	4139	5054	30.8	23.7		
C-C_5H_8	E	4163	5033	30.8			200

APPENDIX G-2

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in D_2O at 25°C.

Solute	Theo./Exp.	ΔG	-ΔH	-ΔS	$\bar{V}_2$	Reference
He	T	6912	622	25.3	17.5	
Ne	T	6617	1195	26.2	18.7	
Ar	T	6267	2698	30.1	26.4	
	E	6227	3123	31.4		184
Kr	T	6030	3477	31.9	30.4	
Xe	T	5661	4493	34.1	35.2	
Rn	T	5124	5991	32.3	43.0	
H_2	T	6691	1253	26.7	19.8	
D_2	T	6674	1271	26.7	19.8	
N_2	T	6923	2595	31.9	32.6	
O_2	T	6405	2650	30.4	27.5	
CO	T	6860	2789	32.4	33.6	
NO	T	6258	2706	30.1	26.4	
CO_2	T	5983	4401	34.8	38.1	
SF_6	T	6449	7566	47.0	78.5	

APPENDIX G-2 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in D_2O at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\overline{V}_2$	Reference
$C_{10}H_{22}$	T	6678	12747	65.2	154.0	
CH_3OH	T	- 836.3	11407	35.5	23.3	
	E		10830			193,194
C_2H_5OH	T	- 727.5	12471	39.4	34.9	
	E		12830			193,194
C_3H_7OH	T	- 540.5	13489	43.4	48.2	
	E		14110			193,194
C_4H_9OH	T	- 421.5	14567	47.4	62.3	
	E		15140			193,194
$C_5H_{11}OH$	T	- 182.3	15420	51.1	76.4	
	E		15930			193,194
$C_6H_{13}OH$	T	- 63.29	16334	54.6	90.2	
$C_7H_{15}OH$	T	- 141.4	17475	58.1	104.54	
$C_9H_{19}OH$	T	- 425.9	19706	64.7	132.1	
$C_{10}H_{21}OH$	T	- 693.7	20914	67.8	145.9	
$C_2H_2NH_2$	T	- 483.1	12692	40.9	40.3	
C_6H_6	T	3292	7807	37.2	38.4	
	E	3352	7761	37.3		200

APPENDIX G-2 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in D_2O at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\overline{V}_2$	Reference
CF_4	T	7414	4420	39.7	56.1	
CCl_4	T	4366	9506	46.5	71.4	
N_2O	T	6589	4885	38.5	50.3	
CS_2	T	3279	8360	39.0	43.8	
H_2S	T	1680	7909	32.2	20.7	
CH_4	T	6277	3342	32.3	31.9	
	E	6276	3366	32.2		166
C_2H_6	T	6107	4807	36.6	43.5	
	E	6071	4335	34.9		166
C_3H_8	T	6219	5944	40.8	56.6	
	E	6203	5776	40.2		163
C_4H_{10}	T	6360	7025	44.9	70.7	
	E	6369	6958	44.7		166
C_5H_{12}	T	6383	8113	48.6	84.2	
	E	5922	6549	41.8		200
C_6H_{14}	T	6467	8983	51.8	96.6	
C_7H_{16}	T	6575	9906	55.3	110.8	

APPENDIX G-2 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in D_2O at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$	Reference
$C_6H_5CH_3$	T	3366	8986	41.4	51.5	
	E	3430	9099	42.0		200
$C_6H_5C_2H_5$	T	3510	9868	44.9	63.36	
$m\text{-}C_6H_4(CH_3)_2$	T	3458	9867	44.7	62.6	
$p\text{-}C_6H_4(CH_3)_2$	T	3464	9861	44.7	62.6	
$i\text{-}C_6H_5C_3H_7$	T	3742	10194	46.7	70.5	
$c\text{-}C_6H_{12}$	T	5185	7681	43.2	61.8	
	E	5196	7608	43.0		200
$c\text{-}C_6H_{10}$	T	4382	7807	40.9	52.3	
	E	4436	7641	40.5		200
$1,4\text{-}c\text{-}C_6H_8$	T	3668	7555	37.6	40.5	
	E	3667	7381	37.1		200
$c\text{-}C_7H_8$	T	3245	8297	38.7	42.7	
	E	3254	7899	37.4		200
$c\text{-}C_5H_{10}$	T	3647	6780	35.0	32.8	
	E	3634	7084	36.0		200
$c\text{-}C_5H_8$	T	4137	5129	31.1	23.9	
	E	4179	5627	32.9		200

APPENDIX G-3

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in Methanol at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
He	T	5643	- 690	16.6	30.5
	E	5764	-1817	13.24	
Ne	T	5161	71.4	17.6	30.4
	E	5579	-1143	14.9	
Ar	T	4368	1600	20.0	37.5
	E	4567	206	16.0	
Kr	T	3947	2381	21.2	41.1
Xe	T	3422	3337	22.7	45.5
H_2	T	5301	- 63.64	17.6	32.4
N_2	T	4853	1174	20.2	46.5
	E	4858	- 120	15.9	
O_2	T	4467	1505	20.0	39.1
	E	4614	229	16.24	
CO	T	4793	1305	20.5	47.6
	E	4672	- 157	16.2	
CO_2	T	3572	3231	22.8	49.2
	E	3074	2555	18.9	
SF_6	T	2632	11476	47.3	93.2

APPENDIX G-3 (CONT'D)

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
CF_4	T	4351	2761	23.9	72.4
CH_4	T	4199	2088	21.1	43.8
	E	4175	862	16.9	
C_2H_6	T	3583	3423	23.5	55.8
C_3H_8	T	3283	4311	25.5	70.3
C_4H_{10}	T	3020	5133	27.4	86.0
C_5H_{12}	T	2679	6015	29.2	100.6
	E		5485[h]		
C_6H_{14}	T	2473	6653	30.6	114.3
	E		6448[h]		
C_7H_{16}	T	2255	7334	32.2	129.8
	E		7464[h]		
H_2O	T	- 893.6	8278	24.8	- 1.33
D_2O	T	- 924.2	8320	24.8	- 1.49

a) See reference 190
b) See reference 188
c) See reference 186
d) See reference 155
e) See reference 187
f) See reference 191
g) See reference 192
h) See reference 193
i) All experimental values for this solvent were taken from reference 196 unless otherwise noted.

* Where T appears no experimental values were available, the units are ΔG (cal/mole), ΔH (cal/mole), ΔS (cal/mole deg.) and $\bar{V}_2$ (cc/mole).

APPENDIX H*

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in Non-Polar Solvents at 25°C.

H-1 CCl_4

H-2 $n\text{-}C_6H_{14}$

H-3 $c\text{-}C_6H_{12}$

H-4 C_6H_6

*All Thermal Units are Calories and Volumes are cc/mole.

APPENDIX H-1

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in CCl_4 at 25°C.

Theo./Exp.*	Solute	ΔG	-ΔH	-ΔS	$\overline{V}_2$
T	He	5185	-1209	13.3	33.1
T	Ne	4586	- 330	14.3	33.2
T	Ar	3691	1124	16.2	42.0
E		3914	103	13.5	44[e,f]
T	Kr	3262	1812	17.0	46.5
T	Xe	2775	2596	18.0	52.3
T	H_2	4774	- 562	14.1	35.5
E		4741	-1340	11.4	38[a,e,f]
T	D_2	4736	- 509	14.2	35.3
E		4752	-1287	11.6	
T	N_2	4235	483	15.8	51.7
E		4350	- 564	12.7	52.5[e]
T	O_2	4103	574	15.7	45.0
E		3984	- 8	13.3	45[a]
T	CO	4191	565	16.0	53.1
E		4171	- 302	13.0	53[a]
T	CO_2	2920	2440	18.0	56.3
E		2698			48[e]
T	SF_6	2150	4108	21.0	106.9
E		2981	1662	15.6	104.0[b]
T	CF_4	3783	1512	17.8	81.5
E		3993	- 141	12.9	79.7[e]

APPENDIX H-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in CCl_4 at 25°C.

Theo./Exp.*	Solute	ΔG	-ΔH	-ΔS	$\bar{V}_2$
T	CH_4	3552	1436	16.7	49.4
E		3468	714	14.0	52[a]
T	C_2H_6	2998	2425	18.2	63.9
E		2294	2630	16.5	65.9[d]
T	C_3H_8	2816	2888	19.1	81.0
T	C_4H_{10}	2690	3262	20.0	99.2
T	C_7H_{16}	2353	4210	22.01	149.7
E					149.1[a]
T	SO_2	1256	-4718	20.0	47.6
E					54[a]
T	Br_2	-85.74	6664	22.1	49.0
E					54.8[c]
T	H_2O	2623	2370	16.8	24.0
E^m		2167	5101	24.4	
T	D_2O	2585	2422	16.8	23.8
E^m		2163	5402	25.4	
T	CH_3OH	5183	- 716	15.0	63.8
E					45.2[g]
T	C_2H_5OH	2918	2611	18.5	69.6
E					59.9[g]
T	C_3H_7OH	1466	4815	21.1	80.9
E					76.6[g]

APPENDIX H-1 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in CCl_4 at 25°C.

Theo./Exp.*	Solute	ΔG	-ΔH	-ΔS	$\bar{V}_2$
T	C_4H_9OH	419.9	6451	23.0	94.9
E					95.1[g]
T	$C_5H_{11}OH$	- 124.2	7375	24.3	110.5
E					111.9[g]
T	$C_6H_{13}OH$	- 596.3	8186	25.5	126.1
T	$C_7H_{15}OH$	-1179	9150	26.7	142.2
E					145.1[g]
T	$C_8H_{17}OH$	-1649	9943	27.8	157.8
E					163.0[g]
T	$C_9H_{19}OH$	-2150	10777	28.9	173.8

APPENDIX H-2

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in n-C_6H_{14} at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	ΔC_p	$\bar{V}_2$
He	T	4730	-1094	12.2	11.9	40.5
	E	4890	-1920	10.0		42.3[i]
Ne	T	4170	- 265	13.1	9.91	39.8
	E	4682	-1348	11.2		
Ar	T	3320	1085	14.8	8.71	48.4
	E	3547	646	14.1		51.5[i]
Kr	T	2924	1710	15.5	8.18	52.8
	E	2943	1130	13.7		
Xr	T	2479	2413	16.4	7.69	58.6
	E	2165	2556	15.8		61.25[i]
H_2	T	4335	- 480	12.9	11.0	42.6
	E	4365	-1219	10.0		
D_2	T	4300	- 430	13.0	10.8	42.3
N_2	T	3792	490	14.4	12.2	59.5
	E	3892				62.8[i]
O_2	T	3413	965	14.7	9.36	50.3
	E	3701				55.7[i]
CO	T	3749	565	14.5	12.4	61.0
CO_2	T	3886	452	14.6	14.6	71.7

APPENDIX H-2 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in n-C_6H_{14} at 25°C.

Solute	Thero./Exp.*	ΔG	-ΔH	-ΔS	ΔC_p	$\overline{V}_2$
C_4H_{10}	T	2369	2918	17.7	15.3	109.2
H_2O	T	2427	2195	15.5	1.98	27.7
	E	2420[n]				
D_2O	T	2393	2243	15.6	1.83	27.5
SF_6	T	1896	3641	18.6	14.8	117.0
CF_4	T	3342	1389	15.9	16.0	91.3
CH_4	T	3180	1363	15.2	9.64	56.3
	E	3135	539	12.3	-	56.8[h]
C_2H_6	T	2665	2238	16.5	10.5	71.4
	E	2039	-	-	-	69.3[d]
C_3H_8	T	2490	2621	17.1	12.8	89.7

APPENDIX H-3

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in c-C_6H_{12} at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\overline{V}_2$
He	T	5152	-1225	13.2	38.4
	E	5340	-2421	9.8	
Ne	T	4528	- 322	14.1	38.3
	E	5111	-1461	12.2	
Ar	T	3601	1149	15.9	48.0
	E	3860	218	13.7	
Kr	T	3164	1836	16.8	53.0
	E	3180	831	13.5	
Xe	T	2671	2615	17.7	59.4
	E	2309	2091	14.8	
H_2	T	4722	- 561	14.0	41.0
	E	4615	-1240	11.3	
N_2	T	4164	484	15.6	59.0
	E	4254	- 511	12.6	
O_2	T	3712	1015	15.9	49.9
	E	3961	- 58	13.1	-
CO	T	4120	565	15.7	60.6
	E	4098	- 202	13.1	
CO_2	T	2823	2449	17.7	63.8
	E	2891	1327	14.1	-

APPENDIX H-3 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in c-C_6H_{12} at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
SF_6	T	2099	400	20.5	119.5
	E	3091	1377	15.0	101.4[k]
CF_4	T	3722	1465	17.4	92.0
	E	4073	- 119	13.3	87.4[k]
CH_4	T	3374	1571	16.6	55.9
	E	3390	588	13.3	
C_2H_6	T	2909	2418	17.9	72.3
	E	2220	2621	16.2	-
C_3H_8	T	2741	2844	18.7	91.2
C_4H_{10}	T	2634	3176	19.5	111.2
H_2O	T	2527	2400	16.5	27.8
	E^m	2652	6335	30.1	-
D_2O	T	2488	2453	16.6	27.6
	E^m	2624	6725	31.4	
CH_3OH	T	5157	- 760	14.8	69.5
	E				44.25[j]
C_2H_5OH	T	2847	2581	18.2	75.7
	E				66.5[j]
C_3H_7OH	T	1386	4761	20.6	87.6
	E				81.5[j]

APPENDIX H-3 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in c-C_6H_{12} at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
C_4H_9OH	T	349.6	6356	22.5	102.6
	E				99.4[j]
$C_5H_{11}OH$	T	- 175.3	7234	23.7	119.2
	E				114.7[j]
$C_6H_{13}OH$	T	- 625.9	7998	24.7	135.8
	E				131.8[j]
$C_8H_{17}OH$	T	-1631	9652	26.9	169.3
	E				165.0[j]
$C_{10}H_{21}OH$	T	-2598	11212	28.9	208.3
	E				198.4[j]

APPENDIX H-4

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in C_6H_6 at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
He	T	5398	-1643	12.6	32.7
	E	5611	-2396	10.8	
Ne	T	4811	- 776	13.5	33.2
	E	5391	-2984	8.07	
Ar	T	3969	570	15.2	42.7
	E	4167	- 297	13.0	43[e]
Kr	T	3565	1211	16.0	47.5
	E	3496	431	13.7	
Xe	T	3101	1940	16.9	53.7
	E	2637	1695	14.5	
H_2	T	5007	-1033	13.3	35.4
	E	4895	-1519	11.3	35.2[e]
D_2	T	4969	- 978	13.4	35.3
	E	4878	-1478	11.4	34[f]
N_2	T	4548	- 171	14.7	52.3
	E	4571	-1016	11.9	52.6[d]
O_2	T	4082	424	15.1	44.3
	E	4213	- 409	12.8	46[a]

APPENDIX H-4 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in C_6H_6 at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
CF_4	T	4205	584	16.1	83.0
	E	4421	- 540	13.0	83.2[e,h]
CH_4	T	3861	806	15.7	50.3
	E	3660	305	13.3	52[d,e,a]
C_2H_6	T	3364	1661	16.9	65.4
	E	2493	2200	15.7	66[d]
C_3H_8	T	3237	1979	17.5	82.9
	E				91.2[i]
C_4H_{10}	T	3165	2209	18.0	101.5
	E				105.0[i]
SO_2	T	1563	4130	19.1	49.6
	E				48[a]
C_2H_2	T	3549	1379	16.5	63.5
	E				51[a]
C_2H_4	T	3297	1737	16.9	62.8
	E	2604	2151	16.0	61[a]
H_2O	T	2814	2038	16.27	24.7
	E	1364	5578	23.28	
D_2O	T	2776	2091	16.33	24.5

APPENDIX H-4 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in C_6H_6 at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\overline{V}_2$
CO	T	4510	- 103	14.8	53.8
	E	4332	- 635	12.4	52[a]
NO	T	4104	379	15.0	43.2
CO_2	T	3259	1746	16.8	57.6
	E	2745	2230	16.7	
SF_6	T	2645	3007	19.0	109.6
	E	3518	778	14.4	105.5[b]
CH_3OH	T	5527	1478	13.6	64.1
	E				41.3[j]
C_2H_5OH	T	3294	1809	17.1	71.3
	E				60.95[j]
C_3H_7OH	T	1879	3939	19.5	83.4
	E				76.9[j]
C_4H_9OH	T	870	5486	21.3	98.2
	E				94.2[j]
$C_5H_{11}OH$	T	364.7	6309	22.4	114.3
	E				110.0[j]
$C_6H_{13}OH$	T	- 71.76	7024	23.3	130.4
	E				128.1[j]

APPENDIX H-4 (CONT'D)

Comparison of Theoretical and Experimental Thermodynamic Properties of Solutes Dissolved in C_6H_6 at 25°C.

Solute	Theo./Exp.*	ΔG	-ΔH	-ΔS	$\bar{V}_2$
$C_7H_{15}OH$	T	- 620.8	7897	24.4	147.0
$C_8H_{17}OH$	T	-1061	8605	25.3	163.0
	E				161.8[j]
$C_9H_{19}OH$	T	-1533	9356	26.2	179.4
$C_{10}H_{21}OH$	T	-2022	10128	27.2	195.4
	E				195.45

a) See reference 195
b) See reference 197
c) See reference 198
d) See reference 199
e) See reference 201
f) See reference 202
g) See reference 203
h) See reference 204
i) See reference 205
j) See reference 206
k) See reference 207
l) All values unless otherwise noted are given in reference 196.

*Where only T appears no experimental values were available, the units are ΔG (cal/mole), ΔH (cal/mole), ΔS (cal/mole deg.), and $\bar{V}_2$ (cc/mole).

m) See reference 229
n) See reference 222
o) See reference 241

APPENDIX I

Best Fit Coefficients for the Solubility of Various Solutes in H_2O.

APPENDIX I

Best Fit Coefficients for the Solubility of Various Solutes in H_2O.

$(\Delta G_s = A + BT + CT^2)$

Solute	Reference	Temperature Range	A	B	C
He	147	277-327	-6480.7	65.675	-0.068089
He	149	288-310	1780.2	10.135	0.025080
He^3	156	273-313	-4544.5	53.642	-0.049588
He^4	156	273-313	-4736.5	55.004	-0.052080
He	157	273-313	-4584.5	53.882	-0.050024
Ne	147	282-315	-4229.3	48.058	-0.035601
Ne	149	288-310	-10052	88.002	-0.10397
Ne	157	273-313	-6133.0	61.381	-0.058773
Ar	158	278-298	-12740	97.166	-0.11200
Ar	147	283-322	-8748.2	70.031	-0.065784
Ar	149	288-310	-7562.7	62.786	-0.054926
Ar	160	278-303	-9540.1	75.360	-0.074857
Ar	174	278-298	-10615	82.874	-0.088000
Ar	175	273-303	-9297.0	74.523	-0.075000
Ar	180	272-303	-18716	141.68	-0.19500
Ar	181	278-293	34718	-233.06	0.46400
Ar	182	273-303	-11726	91.164	-0.10400
Ar	185	278-298	-18308	136.11	-0.18000

APPENDIX I (CONT'D)

Best Fit Coefficients for the Solubility of Various Solutes in H_2O.

($\Delta G_s = A + BT + CT^2$)

Solute	Reference	Temperature Range	A	B	C
Kr	147	279-331	-8597.7	66.162	-0.058208
Xe	147	285-321	-9139.4	65.537	-0.053877
H_2	148	285-327	-5104.3	53.122	-0.046348
N_2	148	285-314	-8421.1	70.034	-0.064572
N_2	160	278-303	-9575	78.205	-0.078857
N_2	173	273-298	-10259	83.705	-0.089714
N_2	175	273-298	-12180	96.355	-0.11029
N_2	178	278-303	-9239.3	75.392	-0.073143
N_2	179	273-298	-14245	111.04	-0.13657
O_2	148	285-331	-10105	79.109	-0.080454
O_2	159	273-308	-10225	80.098	-0.082381
O_2	160	283-303	-10330	80.929	-0.084000
O_2	173	273-298	-9576.6	75.812	-0.075429
O_2	174	278-298	-10007	78.644	-0.080000
O_2	175	273-303	-9462.0	74.781	-0.073143
O_2	176	273-303	-9712.4	76.226	-0.075143
O_2	177	273-303	-14399	109.67	-0.13457

APPENDIX I (CONT'D)

Best Fit Coefficients for the Solubility of Various Solutes in H_2O.

($\Delta G_s = A + BT + CT^2$)

Solute	Reference	Temperature Range	A	B	C
CO_2	148	286-307	-13584	90.292	-0.10065
H_2Se	161	298-314	-7158.2	48.284	-0.038163
CF_4	147	279-312	-9893.6	81.419	-0.078244
C_2H_4	148	286-317	-10615	76.998	-0.076433
CH_4	148	285-319	-13592	101.30	-0.11601
CH_4	152	278-308	-10310	79.178	-0.079000
CH_4	166	278-298	-9055.4	70.503	-0.064000
CH_4	151	278-318	-10603	81.565	-0.083750
CH_4	169	274-312	-11482	87.556	-0.094056
C_2H_6	148	285-314	-15545	111.24	-0.12894
C_2H_6	152	278-308	-15271	106.90	-0.11800
C_2H_6	166	278-298	-12433	87.269	-0.084000
C_2H_6	151	278-318	-16984	118.81	-0.13875
C_2H_6	169	274-312	-15666	110.17	-0.12475
C_3H_8	148	285-322	-15814	109.80	-0.12021
C_3H_8	152	278-308	-14188	96.899	-0.095000
C_3H_8	163	278-323	-18361	125.47	-0.14427

APPENDIX I (CONT'D)

Best Fit Coefficients for the Solubility of Various Solutes in H_2O.

$(\Delta G_s = A + BT + CT^2)$

Solute	Reference	Temperature Range	A	B	C
C_3H_8	151	278-318	-20893	143.57	-0.17625
C_3H_8	169	292-302	-5482.9	39.300	-
C_4H_{10}	148	284-313	-15662	107.21	-0.11158
C_4H_{10}	152	278-308	-19164	129.19	-0.14600
C_4H_{10}	163	278-323	-21639	145.48	-0.17325
C_4H_{10}	166	278-298	-17653	118.73	-0.12800
C_4H_{10}	151	278-318	-24641	165.93	-0.20750
C_4H_{10}	169	292-302	-5930.5	41.200	-
iC_4H_{10}	151	278-318	-17297	119.73	-0.13375
$t\text{-}C_5H_{12}$	151	278-318	-36397	242.74	-0.32833
C_6H_6	166	283-323	-6961.6	32.173	0.0090000
C_6H_6	164	273-338	-18040	107.08	-0.11820
C_6H_6	170	278-315	-17363	102.05	-0.10892
C_6H_6	171	273-318	-18888	112.59	-0.12683
C_6H_6	172	290-336	-16918	99.603	-0.10544
$C_6H_5CH_3$	151	283-322	-26682	159.62	-0.19711
$C_6H_5CH_3$	170	278-308	-20673	120.93	-0.13490

APPENDIX I (CONT'D)

Best Fit Coefficients for the Solubility of Various Solutes in H_2O.

$(\Delta G_s = A + BT + CT^2)$

Solute	Reference	Temperature Range	A	B	C
$m\text{-}C_6H_{14}(CH_3)_2$	170	273-312	-25174	147.69	-0.17347
$p\text{-}C_6H_4(CH_3)_3$	170	283-315	-21902	125.90	-0.13696
$C_6H_5C_2H_5$	170	273-315	-22092	127.09	-0.13861
$i\text{-}C_6H_5\text{-}C_3H_7$	165	298-353	-21439	122.68	-0.12887

APPENDIX J

Best Fit Coefficients for the Solubility of Various Solutes in D_2O.

APPENDIX J

Best Fit Coefficients for the Solubility of Various Solutes in D_2O.

$$(\Delta G_s = A + BT + CT^2)$$

Solute	Reference	Temperature Range	A	B	C
Ar	184	278-298	-12723	95.760	-0.10800
CH_4	166	278-298	-12008	89.825	-0.096000
C_2H_6	166	278-298	-23892	166.09	-0.22000
C_3H_8	163	277-323	-19098	129.54	-0.14986
C_4H_{10}	163	277-323	-23135	154.63	-0.18733
C_4H_{10}	166	278-298	-17981	118.64	-0.12400
C_6H_6	166	283-323	-10781	57.688	-0.033000

APPENDIX K*

Experimental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.

*All Thermal Units are Calories.

APPENDIX K

Experimental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.*

Solvent	ΔG	-ΔH	ΔS	Reference
pentane	2469	2100	1.2	219
hexane	2237	478	9.11	220
	2479			221
	2420			222
heptane	2116	2843	16.6	219
	2215	411	8.81	220
	2438			223
octane	2160	456	8.80	220
	2352			222
nonane	2383			223
decane	2373	2656		223
undecane	2342	2627		223
dodecane	2332	2101		223
tridecane	2343	1276		223
hexadecane	2268	2343		223
	1947	185	7.15	220
2-methylbutane	2538	5579	27.2	219
	2346	710	10.3	220
2,3-dimethylbutane	2252	470	9.13	220
2-methylhexane	2198	456	8.90	220
2,2,3-trimethyl-butane	2123	617	9.19	220
2,2,4-trimethyl-pentant	2062	562	8.80	220
2,4-dimethylhexane	2132	149	7.65	220
2,6-dimethylheptane	2127	846	9.97	220

APPENDIX K (CONT'D)

Experimental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.

Solvent	ΔG	-ΔH	ΔS	Reference
2-methyloctane	2141	811	9.90	220
3-methyloctane	2154	321	8.30	220
2-methyl-2-butane	1521^{20}			220
2,3-dimethyl-1-butene	1384^{20}			220
1-hexene	1362^{20}			220
1-heptene	1764	3293	16.9	220
1-undecane	1638	4443	20.4	220
benzene	1556	4191	19.3	219
	1413	6104	25.2	220
	1345			221
	1381			222
	1420	5982	24.8	225
	1425			226
	1369			227
	1425	5909	24.6	228
	1374			230
	1364	5578	23.3	241
toluene	1460	5536	23.5	220
	1434			222
	1470	5882	24.7	225
	1643			226
	1529	4434	20.0	228
	1432	6916	28.0	229
	1403			231
ethylbenzene	1484	5284	22.7	220
	1492	6140	25.6	228
o-xylene	1486			222

APPENDIX K (CONT'D)

Experimental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.

Solvent	ΔG	-ΔH	ΔS	Reference
m-xylene	1504		23.1	222
	1440	5447		220
p-xylene	1370			222
styrene	1325	4479	19.5	225
1,3,5-trimethyl-benzene	1556	5212	22.7	220
cumene	1530	5193	22.6	220
n-butylbenzene	1382	5178	22.0	228
	1412	5207	22.2	220
s-butylbenzene	1440	5298	22.6	220
t-butylbenzene	1490	5457	23.3	220
chlorobenzene	1485	2536	13.5	225
	1654	6070	25.9	228
	1618			226
bromobenzene	1522	5544	23.7	228
	1508			226
Iodobenzene	1663	5433	23.8	228
	1651			226
o-dichlorobenzene	1628	4931	22.0	228
	1645			226
cyclopentane	2215	1420	12.2	220
methylcyclopentane	2186	2643	16.2	220
ethylcyclopentane	2159	2641	16.1	220

APPENDIX K (CONT'D)

Expermental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.

Solvent	ΔG	-ΔH	ΔS	Reference
m-xylene	1504			222
	1440	5447	23.1	220
p-xylene	1370			222
styrene	1325	4479	19.5	225
1,3,5-trimethyl-benzene	1556	5212	22.7	220
cumene	1530	5193	22.6	220
n-butylbenzene	1382	5178	22.0	228
	1412	5207	22.2	220
s-butylbenzene	1440	5298	22.6	220
t-butylbenzene	1490	5457	23.3	220
chlorobenzene	1485	2536	13.5	225
	1654	6070	25.9	228
	1618			226
bromobenzene	1522	5544	23.7	228
	1508			226
iodobenzene	1663	5433	23.8	228
	1651			226
o-dichlorobenzene	1628	4931	22.0	228
	1645			226
cyclopentane	2215	1420	12.2	220
methylcyclo-pentane	2186	2643	16.2	220
ethylcyclo-pentane	2159	2641	16.1	220

APPENDIX K (CONT'D)

Experimental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.

Solvent	ΔG	-ΔH	ΔS	Reference
isopropycyclo-pentane	2170	2690	16.3	220
butylcyclo-pentane	2138	2364	15.1	220
cyclohexane	2236	1503	12.5	220
	2621			221
	2652	6335	30.1	229
	2835			231
methylcylo-hexane	2167	2901	17.0	220
cyclohexene	1734	5749	25.1	220
cycloheptatriene	1396	7817	30.9	220
decaline	2314	1502	12.8	220
bicyclo[221]-hepta-2,5-diene	1719	5913	25.6	220
chloroform	985	-	-	225
chloroform	982	-	-	227
carbon disulfide	2544	-	-	225
1,2-dichloro-ethane	673	5499	-	227
tetrachloroethylene	2013	2316	14.5	224

APPENDIX K (CONT'D)

Experimental Thermodynamic Solution Properties of H_2O Dissolved in Various Solvents Evaluated at 25°C.

Solvent	ΔG	-ΔH	ΔS	Reference
CCl_4	2172	5990	27.4	219
	2057	-	-	222
	2089	2178	14.3	224
	2098	-	-	225
	2167	5101	24.4	229
	2140	-	-	231

*The units are ΔG (cal/mole), ΔH (cal/mole), and ΔS (cal/mole deg).

APPENDIX L*

Experimental Thermodynamic Solution Properties of D_2O Dissolved in Various Solvents Evaluated at 25°C.

*Thermal Units are Calories.

APPENDIX L

Solution Properties of D_2O Dissolved in Various Solvents Evaluated at 25°C.

Solvent	ΔG	-ΔH	ΔS	Ref.
CCl_4	2163	5402	25.4	229
	2180			232
	2139			233
Toluene	1472	6161	25.7	229
	1447			233
cyclohexane	2624	6725	31.4	229
	2708			233

APPENDIX M

VAPOR PRESSURE OF H_2O AND D_2O AS A FUNCTION OF TEMPERATURE.

APPENDIX M

Vapor Pressure of H_2O and D_2O as a Function Of Temperature

t, °C	P_{H_2O},atm [a]	P_{D_2O},atm [b]
5	0.008609	0.007209
10	0.01212	0.01025
15	0.01683	0.01443
20	0.02307	0.02000
25	0.03126	0.02730
30	0.04187	0.03680
35	0.05549	0.04904
40	0.07279	0.06470
45	0.09458	0.08453
50	0.1217	0.1094

a) See reference 137

b) See reference 233

APPENDIX N*

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at $25^{\circ}C$.

*All Thermal Units are Calories.

APPENDIX N

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at 25^oC.

Solute	ΔG	$-\Delta H$	Reference
Hg	3660	11360	215
He	7064	390	167
	6970	1020	150
Ne	6940	1080	167
	6712	1880	150
Ar	6291	3100	167
	6280	2730	150
Kr	5952	3440	167
	6086	3550	150
Xe	5636	4710	167
	5533	4490	150
Rn	5182	5050	150
H_2	6477	1280	150
N_2	6750	2140	150
O_2	6348	2990	150
CO_2	4399	4730	150
CO	4980	3910	150
COS	4671	5800	150
NO	6091	2680	150
N_2O	4587	4840	150
NH_3	1042	5040	162
CH_3Cl	3723	6300	150
CCl_4	4376	6900	150
C_2H_4	5548	3790	150

APPENDIX N (CONT'D)

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at 25°C.

Solute	ΔG	-ΔH	Reference
C_2H_2	4278	3360	150
CH_4	6307	3180	150
C_2H_6	6125	4430	150
CH_3F	4073	4404	257
CH_3Cl	3707	5670	257
CH_3Br	3453	6275	257
CH_3I	3365	6325	257
CH_3OH	-819	11251	257
CH_3Cl	3619	5700	256
C_2H_5Cl	3782	6700	256
C_3H_7Cl	3783	8100	256
C_4H_7Cl	3827	9100	256
C_5H_9Cl	3790	10300	256
CH_3Br	3277	6400	256
C_2H_5Br	4079	7000	256
C_3H_7Br	3522	8600	256
C_4H_9Br	3615	9700	256
$C_5H_{11}Br$	3648	10800	256
CH_3I	3277	6400	256
C_2H_5I	4079	7000	256
C_3H_7I	3522	8600	256

APPENDIX N (CONT'D)

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at 25°C.

Solute	ΔG	-ΔH	Reference
dodecanoic acid	-3249	-	211
tetradecanoic acid	-5224	-	211
hexadecanoic acid	-9435	-	211
octadecanoic acid	-16346	-	211
$C_2H_5NH_2$	- 328	12910	150
$C_3H_7NH_2$	-	13325	212
$C_4H_9NH_2$	-	14111	212
$C_5H_{11}NH_2$	-	14847	212
$C_6H_{13}NH_2$	-	15717	212
NH_3	- 31	8243	216
CH_3NH_2	- 295	10818	216
$C_2H_5NH_2$	- 233	13051	216
$C_3H_7NH_2$	- 127	13370	216
$C_4H_9NH_2$	- 28	14122	216
$C_5H_{11}NH_2$	174	14846	216
$C_6H_{13}NH_2$	235	15717	216
pyridine	- 423	11980	217
2-picoline	- 355	13280	217
3-picoline	- 498	13240	217
4-picoline	- 659	13270	217
2,6-lutidine	- 325	14820	217

APPENDIX N (CONT'D)

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at 25°C.

Solute	ΔG	-ΔH	Reference
2,5-lutidine	- 441	14540	217
2,4-lutidine	- 587	14510	217
3,5-lutidine	- 566	14460	217
pyridine	- 423	11650	218
2-methyl-pyrdine	- 355	12640	218
3-methyl-pyrdine	- 498	12600	218
4-methyl-pyrdine	- 659	12820	218
2-ethylpydine	- 57	13310	218
3-ethylpydine	- 328	12780	218
4-ethylpydine	- 462	12480	218
2,3-dimethyl-pyridine	- 549	13790	218
2,4-dimethyl-pyridine	- 587	14020	218
2,5-dimethyl-pyridine	- 441	14000	218
2,6-dimethyl-pyridine	- 325	14440	218
3,4-dimethyl-pyridine	- 945	13540	218
3,5-dimethyl-pyridine	- 566	13450	218
THF	805	11296	208

APPENDIX N (CONT'D)

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at 25°C.

Solute	ΔG	-ΔH	Reference
2methylTHF	973	12280	208
2,5-dimethyl THF	1355	13456	208
THP	1151	11682	208
1,3-dioxolan	180	9540	208
1,4-dioxan	- 780	11466	208
aziridine	-	11944	209
azetidine	-	14259	209
pyrrolidine	-1206	15193	209
piperdine	- 833	15634	209
hexamethyleneimine	- 634	16314	209
heptamethyleneimine	-	15997	209
N-methylpyrididine	297	15158	209
N-methylpiperidine	382	15720	209
phenol	-2280	13610	213
2-cresol	-1593	14520	214
4-cresol	-1858	14290	214
4-t-butylphenol	-1649	15250	214
4-bromophenol	-2860	16270	213
4-nitrophenol	-6377	18040	213
4-formylphenol	-6199	17130	213

APPENDIX N (CONT'D)

Experimental Free Energies and Heats of Solution of Various Solutes in H_2O at 25°C.

Solute	ΔG	-ΔH	Reference
C_4H_9I	3615	9700	256
$C_5H_{11}I$	3648	10800	256
CH_3COOH	-2429	12620	150,212
C_2H_5COOH	-2201	13504	150,212
C_3H_7COOH	-2085	14221	150,212
2,2,2-trifluorethanol	-30.11	11967	210
2,2,3,3-tetrafluoro-1-propanol	-618.1	13846	210
2,2,3,3,3-pentrafluoro-1-propanol	120.7	12397	210
1,1,1-trifluoro-2-propanol	116.4	12796	210
1,1,1,3,3,3-hexafluoro-2-propanol	506.7	13467	210
dodecanol	197	-	211
tetradecanol	- 230	-	211
pentadecanol	- 721	-	211
hexadecanol	-1438	-	211
heptadecanol	-2530	-	211
HCOOH	-	11233	212
CH_3COOH	-	12620	212
C_2H_5COOH	-	13504	212
C_3H_7COOH	-	14221	212

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VITA

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He is the proud father of three lovely daughters: Barbara Glenn, Felecia Dawn, and Adrienne Suzanne.